

Studies on Novel Binary Accelerator System in Sulfur Vulcanization of Natural Rubber

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ABSTRACT: The synergistic activity of binary accelerator systems in rubber vulcanization is well known. Binary accelerator systems are being widely used in industry and are becoming increasingly popular because of the fact that such mixed systems can effectively prevent prevulcanization, permit the vulcanization to be carried out at a lower temperature in a shorter time, and produce a vulcanizate with superior mechanical properties compared to those of a stock cured with a single accelerator. Thiourea and its derivatives are important secondary accelerators in this context. It is suggested that thiourea containing binary accelerator systems cause rubber vulcanization to proceed by a nucleophilic reaction mechanism. In the present study 1-phenyl-5-*ortho*-, *meta*-, and *para*-tolyl derivatives of 2,4-dithiobiurets, which are more nucleophilic than thiourea and vary in their nucleophilic reactivity, are used as secondary accelerators

along with 2-morpholinothiobenzothiazole in the vulcanization of natural rubber. The results show an appreciable reduction in the cure time for the mixes containing the dithiobiurets compared to the reference mix. These results are indicative of a nucleophilic reaction mechanism in the vulcanization reaction under consideration. These vulcanizates also demonstrate comparatively better tensile properties and good retention of these properties after aging. An attempt is also made to correlate the variation in physical properties to chemical crosslink formation in the various vulcanizates. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3173–3182, 2003

Key words: rubber; vulcanization; mechanical properties; crosslinking

INTRODUCTION

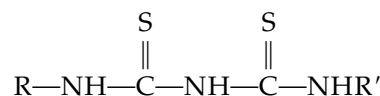
Ever since the initial discovery of Charles Goodyear and Thomas Hancock that small quantities of sulfur used at the time of vulcanization yields the best quality rubber with extra strength, researchers have been fascinated by the infinite possibilities in this field. Binary accelerator combinations can give faster cure rates in rubber vulcanization systems.^{1–9}

The synergistic behavior of these systems is said to be due to the formation of new chemical moieties, which make the curing process easier.^{10–17} The choice of the accelerator in sulfur vulcanization determines the kind of network structure that is produced and consequently the specific material properties. The accelerator that is chosen affects the cure rate and scorch safety, as well as the number and average length of the crosslinks that are formed. The number, distribution, and length of crosslinks influence the physical properties of rubber.

Thiourea (TU) and its derivatives are known for their acceleration activity, and they are being frequently used in mixed accelerator systems in the vulcanization of natural rubber (NR) latex and neoprene

rubber. Philpot¹⁶ showed the high reactivity of TU in the vulcanization of NR latex when used with tetramethyl thiuram disulfide and *N*-cyclohexyl benzothiazyl sulfenamide. Mathew et al.^{11,12} extended this study to different dithiobiuret (DTB) derivatives of TU, and their results agree with the suggestion made by Philpot.¹⁶

As a continuation of this study, we selected *ortho*-, *meta*-, and *para*-tolyl derivatives of DTB (*o*-, *m*- and *p*-DTBs) of the general formula



where R = C₆H₅— and R' = *o*-, *m*-, and *p*-tolyl as secondary accelerators with 2-morpholinothiobenzothiazole (MBS) in the sulfur vulcanization of NR.

We studied the acceleration activity of three different DTBs as secondary accelerators with MBS in the vulcanization of NR. All the mixes showed an appreciable reduction in the optimum cure time compared to A reference formulation. Of the three different DTB derivatives studied, the cure time was found to be lower for *o*- and *p*-DTBs compared to *m*-DTB. The reason for the lowering of the cure time can be related to the higher nucleophilic character of the *o*- and *p*-DTBs. This is because of the +I effect of the methyl

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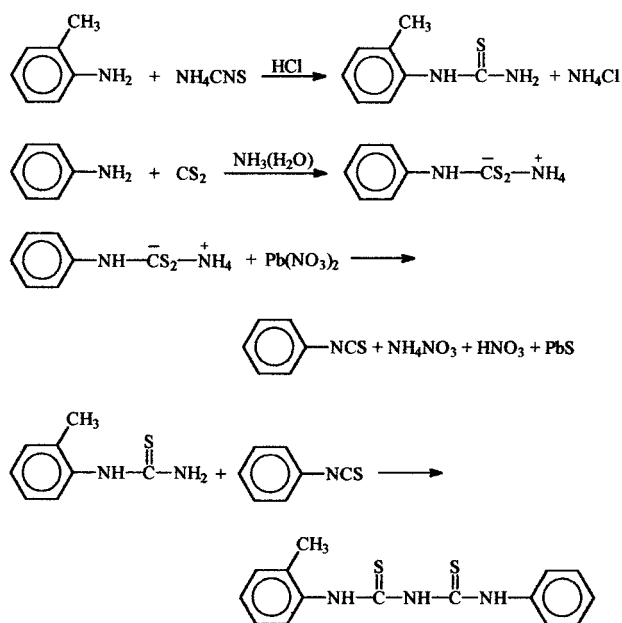
group and the hyperconjugative effect. Reference mixes containing MBS and MBS-DTB were also prepared.

EXPERIMENTAL

Preparation of *o*-, *p*-, and *m*-DTBs

The DTBs were prepared according to Joshua et al.¹⁸ Toluyl TUs were prepared by the interaction of the three different toluidines (*o*-, *p*-, and *m*-) with ammonium thiocyanate in hydrochloric acid.

Ammonium phenyl dithiocarbamate was prepared by the interaction of carbon disulfide and aniline in an ammoniacal medium at 0°C. The product thus obtained was steam distilled with lead nitrate to obtain phenyl isothiocyanate. The latter (0.025 mol) was added dropwise to a stirred solution of tolyl TU (0.025 mol) and powdered sodium hydroxide (0.025 mol) in acetonitrile (15 mL), and the reaction mixture was heated at 60°C for 0.5 h and a clear solution was obtained. This was then diluted with water (150 mL) and filtered and the filtrate acidified with concentrated hydrochloric acid (4 mL, 33%). The crude DTB that was obtained was dissolved in a minimum quantity of 4% aqueous sodium hydroxide to remove any unreacted TU and filtered. The alkaline filtrate on acidification at 0°C afforded the DTB that was recrystallized from ethanol. The reaction pathway is shown below.



Yield of *o*-DTB = 78%

Yield of *p*-DTB = 81%

Yield of *m*-DTB = 71%

Characterization of *o*-, *p*-, and *m*-DTBs

The crude DTB was purified by recrystallizing it in ethanol. Pure samples were analyzed using IR spectroscopy.

IR spectra

The IR spectra of the samples were taken on an FTIR impact 410 spectrometer. The spectra for the *o*-, *p*-, and *m*-DTBs are given in Figures 1, 2, and 3, respectively.

o-DTB

The characteristic absorbance peaks obtained are 3170 (NH stretch), 1595 (NH deformation), 1195 (CH stretch), 2915 (methyl CH stretch), and 3028 cm^{-1} (aromatic CH stretch). This confirms the presence of $\text{NH}_2\text{—CH—CS}$ and a phenyl ring structure in DTB. The characteristic group frequency for the *o*-substituted derivative is 746.75 cm^{-1} .

p-DTB

We obtained characteristic absorbance peaks of 3171 (NH stretch), 1600 (NH deformation), 1175 (CH stretch), and 3020 cm^{-1} (aromatic CH stretch). This confirms the presence of $\text{NH}_2\text{—CH—CS}$ and the phenyl ring structure in DTB. The characteristic group frequency for the *p*-substituted derivative is 818 cm^{-1} .

m-DTB

The characteristic absorbance peaks that were obtained are 3159 (NH stretch), 1595 (NH, deformation), 2917 (methyl CH stretch), and 3027 cm^{-1} (aromatic CH stretch). This confirms the presence of $\text{NH}_2\text{—CH—CS}$ and the phenyl ring structure in DTB. The characteristic group frequencies for *m*-substituted derivatives are 814.9, 754.07, and 691.72 cm^{-1} .

Materials

The NR (ISNR-5) used in the study had a Mooney viscosity (ML 1+4, 100°C) of 85 and was obtained from the Rubber Research Institute of India (Kottayam, India). The MBS was supplied by Bayer India Ltd. (Bombay). Acetonitrile, aniline, toluidine, sodium hydroxide, lead nitrate, carbon disulfide, and ammonia were laboratory reagent grades. The rubber additives zinc oxide, stearic acid, and sulfur were rubber grade.

The formulations of the different mixes used in the present investigation are shown in Table I. Mixes A_1 , D_1 , D_2 , and D_3 are the reference mixes, which contain 10 mmol MBS, and 5 mmol MBS with 1, 2, and 5 mmol of DTB, respectively, as accelera-

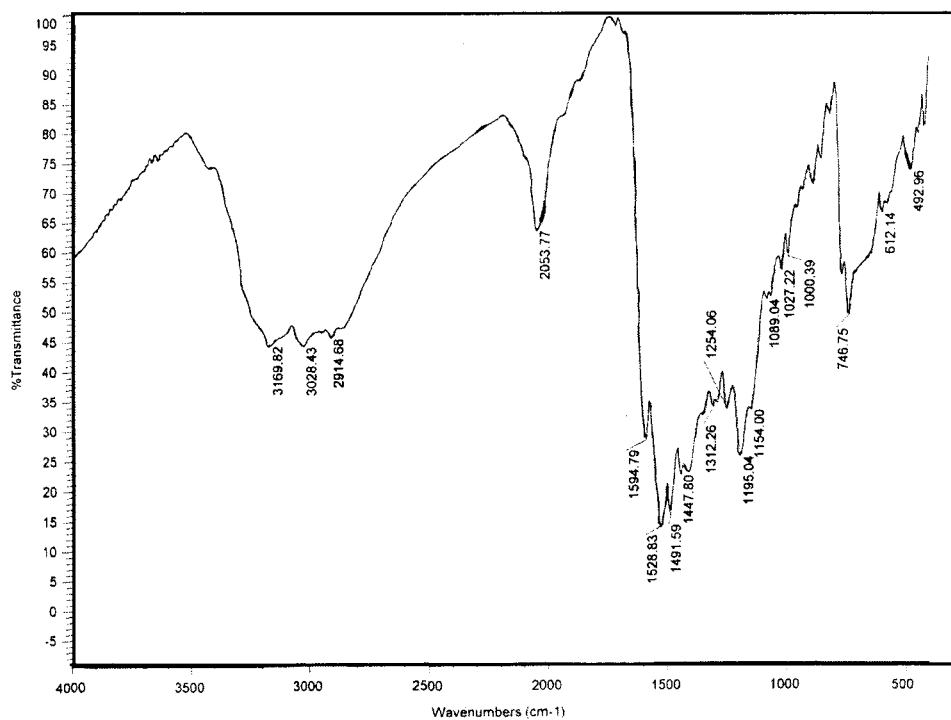


Figure 1 The IR spectrum of *o*-DTB.

tors. Mixes O₁, O₂, and O₃ contain 5 mmol of MBS with 1, 2, and 5 mmol of *o*-DTB, respectively. Mixes P₁, P₂, and P₃ contain 1, 2, and 5 mmol of *p*-DTB, respectively, with 5 mmol of MBS. Mixes M₁, M₂,

and M₃ contain 1, 2, and 5 mmol of *m*-DTB, respectively, with 5 mmol of MBS.

Compounding of the NR was done on a laboratory size two-roll mixing mill (friction ratio = 1:1.4) accord-

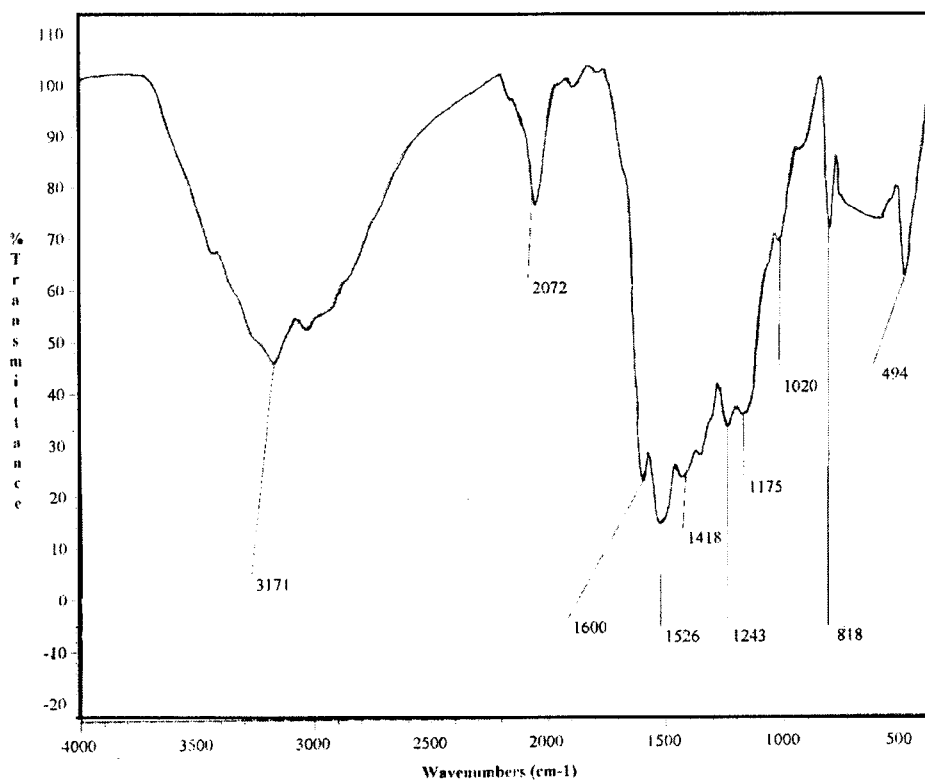


Figure 2 The IR spectrum of *p*-DTB.

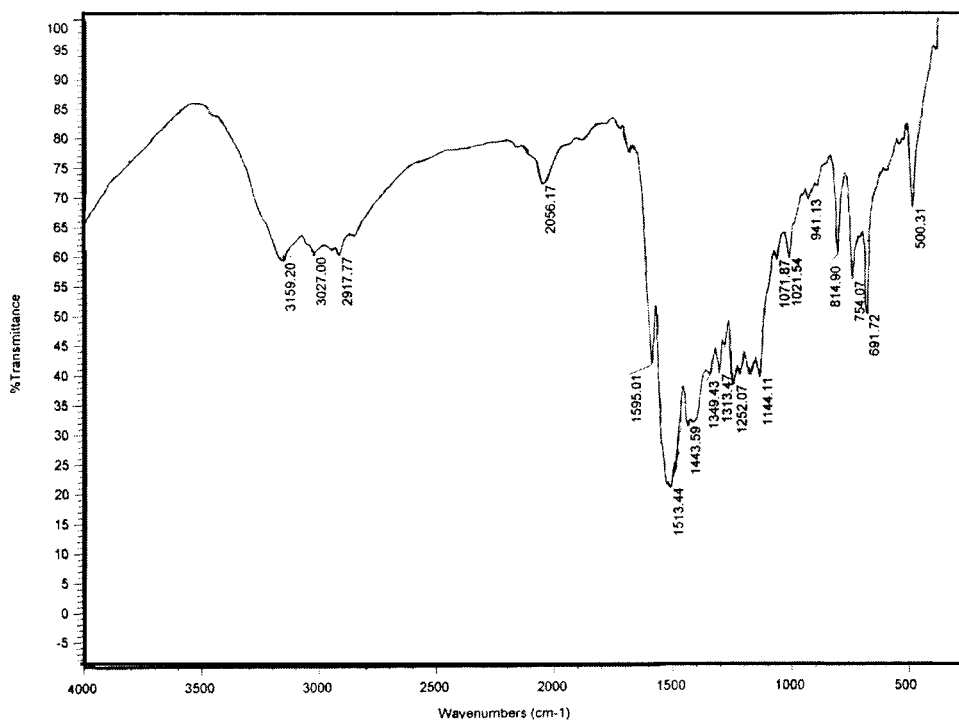


Figure 3 The IR spectrum of *m*-DTB.

ing to ASTM D 15-627. The cure characteristics of the mixes were obtained using a Monsanto Rheometer R 100 at 150°C according to ASTM D 2084-88.

The induction time (t_5) is the time for a one-unit rise above minimum torque (i.e., about 5% vulcanization). The scorch time is the time for a two-unit rise above the minimum torque (i.e., about 10% vulcanization). The cure rate index (CRI) is reported as

$$\text{CRI} = \frac{100}{t_{90} - t_{10}} \quad (1)$$

where t_{90} and t_{10} are the times corresponding to the optimum cure and scorch, respectively. The cure characteristics are reported in Table II and the different cure curves are given in Figures 4, 5, and 6.

The stocks were then vulcanized up to the optimum cure time in an electrically heated hydraulic press at 150°C and a pressure of 120 kg cm⁻². Dumbbell-shaped tensile and angular tear specimens were punched out from the compression molded sheets along the mill grain direction. The tensile properties and the tear resistance of the vulcanizates were determined on a tensile testing machine (TNE series 9200) at a crosshead speed of 500 mm/min according to ASTM D 412-80 and ASTM D 624-81, respectively.

The heat aging resistance of the vulcanizates was evaluated by aging the samples for 48 h at 70°C in a laboratory oven (ASTM D 573). A Shore A type durometer was used to ascertain the hardness of the vulcanizates (ASTM D 676-52).

A Goodrich flexometer conforming to ASTM D 623-88 (method A) was used for measuring heat buildup. The rebound resilience was measured using a Dunlop tripsometer according to ASTM D 1054.

Determination of chemical crosslinks

The chemical crosslink density ($1/2M_c$) was calculated using the Flory-Rehner equation¹⁹:

$$-[\ln(1 - V_r) + V_r + \chi V_r^2] = \frac{\rho_r V_s (V_r)^{1/3}}{M_c} \quad (2)$$

where ρ_r is the density of the test specimen (0.921 g/cm³), V_s is the molar volume of the toluene solvent ($V_s = 106.2$ cm³/mol), χ is the parameter characteristic of the interaction between the rubber and solvent²⁰ ($\chi_{(\text{NR-toluene})} = 0.42$), M_c is the number-average molecular weight of the rubber chains between crosslinks, and V_r is the volume fraction of rubber in the swollen network. Samples of approximately 1-cm diameter, 0.2-cm thickness, and 0.2-g weight were punched out from the central portion of the vulcanizate. These were then allowed to swell in toluene for 48 h. The swollen samples were taken out and weighed. The solvent was removed in a vacuum and the samples weighed again. The V_r value in the swollen network was then calculated by the method reported by Ellis and Welding from the following equation²¹:

TABLE I
Formulation of Mixes Containing MBS, MBS-DTB, and MBS-DPG

Ingredients	O ₁	O ₂	O ₃	P ₁	P ₂	P ₃	M ₁	M ₂	M ₃	A ₁	D ₁	D ₂	D ₃
Natural rubber (phr)	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide (phr)	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid (phr)	2	2	2	2	2	2	2	2	2	2	2	2	2
MBS (phr)	1.26 (5 mmol)	1.26 (5 mmol)	1.26 (5 mmol)	1.26 (5 mmol)	1.26 (5 mmol)	1.26 (5 mmol)	1.26 (5 mmol)	1.26 (5 mmol)	1.26 (5 mmol)	2.52 (10 mmol)	1.26 (5 mmol)	1.26 (5 mmol)	1.26 (5 mmol)
<i>o</i> -DTB (phr)	0.301	0.602	1.505	—	—	—	—	—	—	—	—	—	—
<i>p</i> -DTB (phr)	—	—	—	0.301 (1 mmol)	0.602 (2 mmol)	1.505 (5 mmol)	—	—	—	—	—	—	—
<i>m</i> -DTB (phr)	—	—	—	—	—	—	0.301 (1 mmol)	0.602 (2 mmol)	1.505 (5 mmol)	—	—	—	—
DPG (phr)	—	—	—	—	—	—	—	—	—	—	0.176 (1 mmol)	0.352 (2 mmol)	0.88 (5 mmol)
Sulfur (phr)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE II
Cure Characteristics of MBS-DTB and MBS-DPG
Mixes Cured at 150°C

Mix No.	Torque (dNm)		<i>t</i> ₅ (min)	<i>t</i> ₁₀ (min)	<i>t</i> ₉₀ (min)	Cure Rate Index
	Min	Max				
O ₁	3	29	4.5	5	9	25
O ₂	6	39	3	4	7.5	28.57
O ₃	3.5	32	2	2	5	33.33
P ₁	5	35	5	5	9	25
P ₂	3.5	33	4.5	4.5	8	28.57
P ₃	3.5	32	2	2.5	5.5	33.33
M ₁	4	35	5.5	6	10.5	22.22
M ₂	6.5	36	4.5	4.5	8.5	25
M ₃	3	33	1.5	3	6.5	28.57
A ₁	4	36	11	11.5	16.5	20
D ₁	4	35	12	12.5	18	18.18
D ₂	4	36	8.5	9	14	20
D ₃	5	37	6	6.5	11.5	20

*t*₅, induction time; *t*₁₀, scorch times *t*₉₀, cure time.

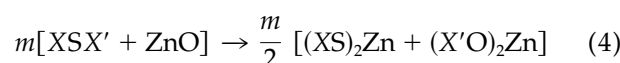
$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}} \quad (3)$$

where *T* is the weight of the test specimen, *D* is the weight of the deswollen test specimen, *F* is the weight fraction of insoluble components, *A*₀ is the weight of the absorbed solvent corrected for the swelling increment, ρ_r is the density of the test specimen (0.921 g/cm³), and ρ_s is the density of the solvent (0.886 g/cm³).

RESULTS AND DISCUSSION

The cure characteristics of the various mixes at 150°C were evaluated. The cure curves obtained are given in Figures 4–6. It can be seen from Table II that the optimum cure time of 16.5 min at 150°C for the system containing 10 mmol MBS is reduced to 9, 9, and 10.5 min by adding 1 mmol of *o*-, *p*-, and *m*-DTB, respectively. The addition of 2 mmol DTB reduces the optimum cure time to more than half that using MBS alone. The cure time of 16.5 min is reduced to 7.5, 8, and 8.5 min by the addition of *o*-, *p*-, and *m*-DTB, respectively. These results clearly indicate the effectiveness of the DTBs as accelerators in the vulcanization of NR using the MBS/sulfur system. Among the three DTBs that we studied, *o*- and *p*-DTBs are more active than *m*-DTB because the *o*- and *p*-DTBs are more nucleophilic in nature. This supports the nucleophilic mechanism for the vulcanization reaction of NR.⁵

A novel probable mechanism for the synergistic activity of *o*-, *p*-, and *m*-DTBs is as follows. MBS reacts with ZnO to form benzothiazyl zinc salt:



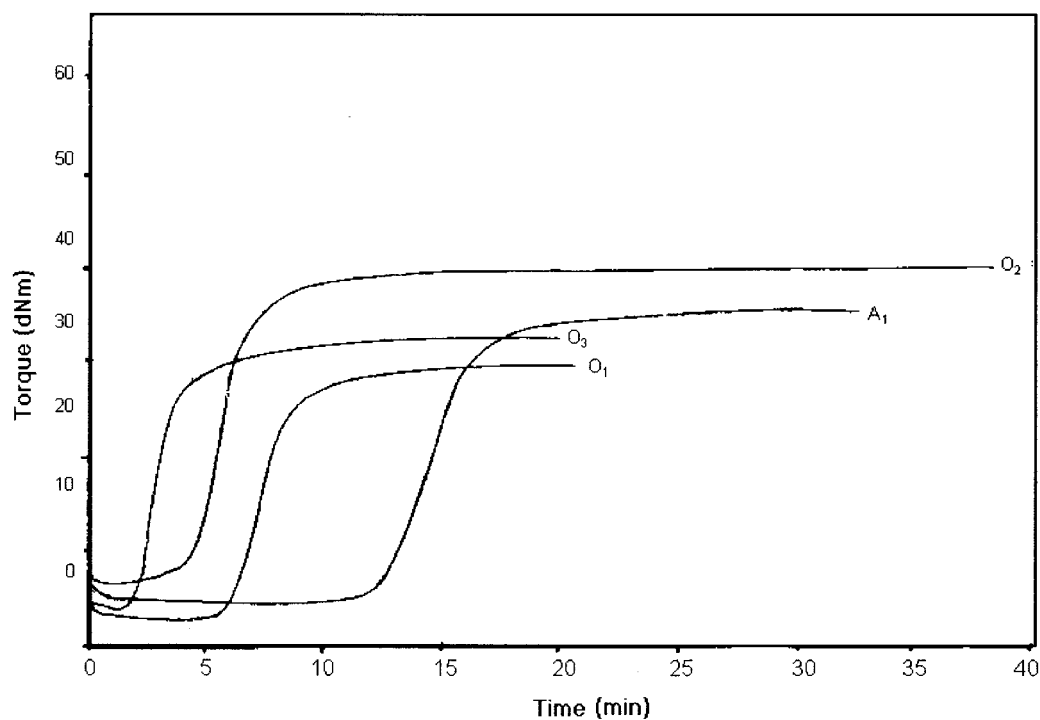
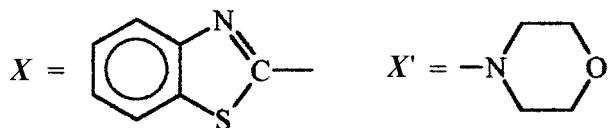
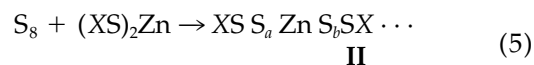


Figure 4 The cure curves of mixes A_1 , O_1 , O_2 , and O_3 .

where $m > 2$ and



Benzothiazyl zinc salt reacts with elemental sulfur to form zinc perthio salt (II):



DTB reacts with MBS to form III:

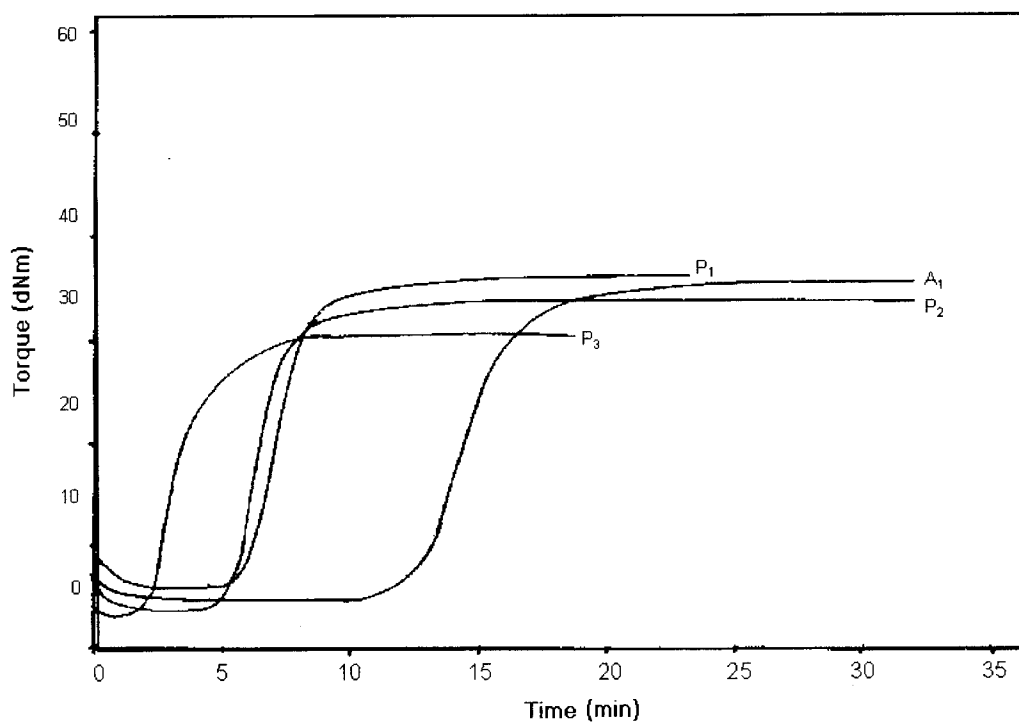


Figure 5 The cure curves of mixes A_1 , P_1 , P_2 , and P_3 .

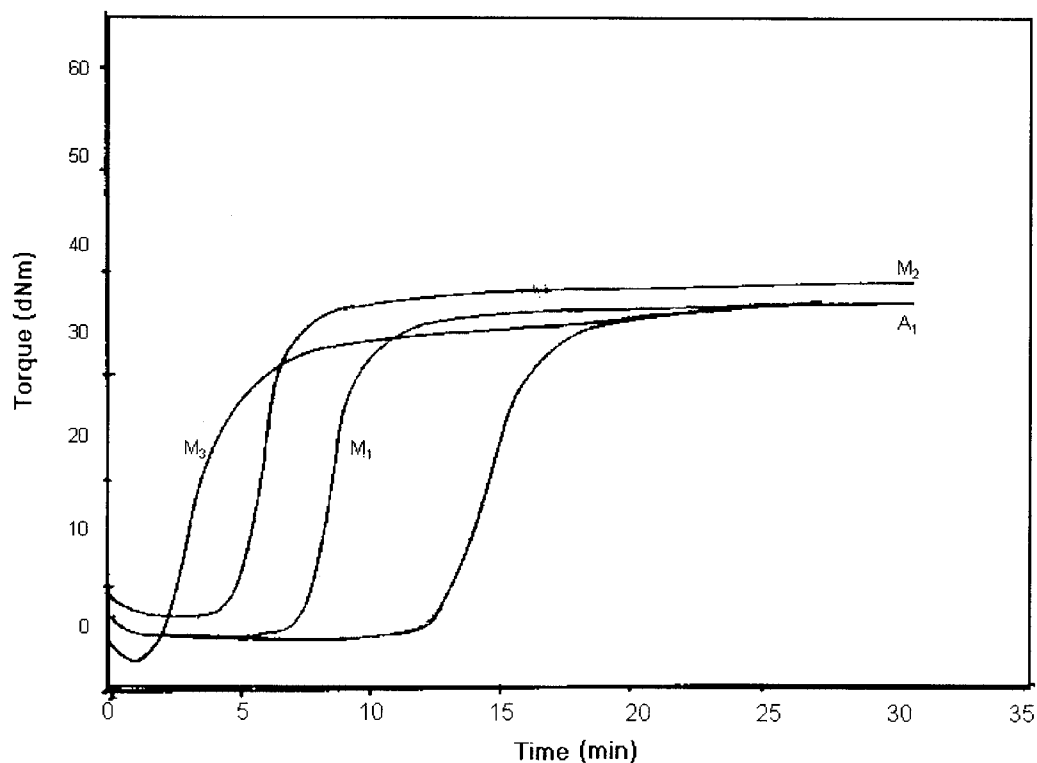
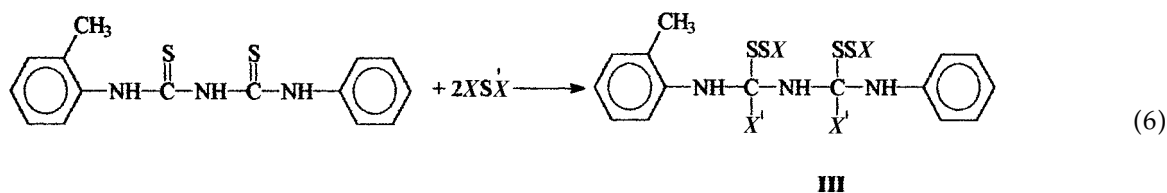
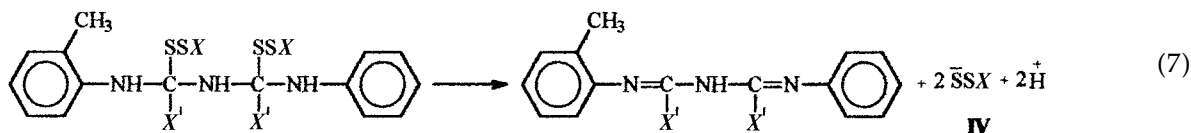


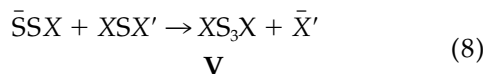
Figure 6 The cure curves of mixes A₁, M₁, M₂, and M₃.



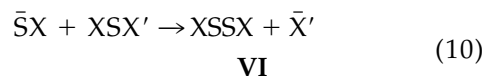
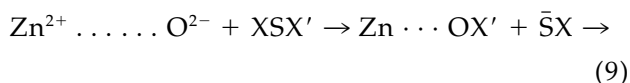
Compound III is stabilized by a proton shift to ZnO and simultaneous elimination of perthioanion (IV):



Trisulfide V (XS₃X) can be formed by the reaction between perthioanion and MBS:



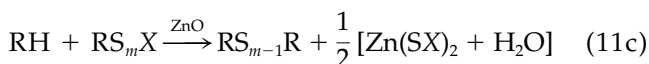
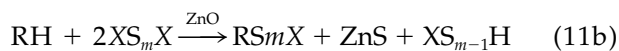
Disulfide VI (XSSX) can be formed by the reaction between MBS and ZnO, which is a slow process:



Participation of disulfide VI and trisulfide V in processes similar to eqs. (8)–(10) lead to the formation of higher polysulfides.

In the presence of *o*-, *p*-, and *m*-DTBs, SX' bond fission in MBS is accelerated, providing an easier and faster route for the formation of polysulfide XS_{*m*}X.

The polysulfide XS_{*m*}X and zinc perthio salt react with rubber hydrocarbon (RH) to form a rubber bound intermediate RS_{*m*}X:



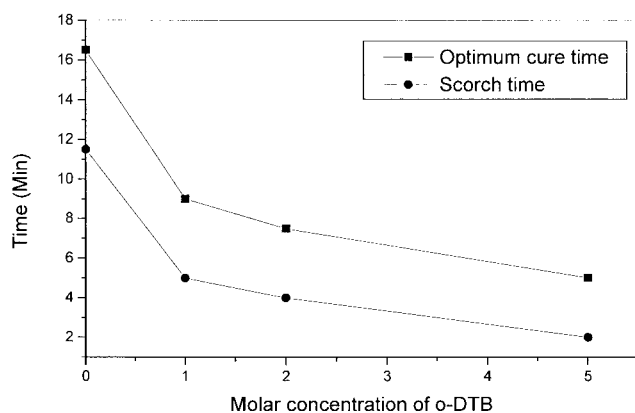
The addition of DTB reduces the cure time to a greater extent. Figure 7(a–c) shows the variation in the optimum cure time and scorch time with varying concentrations of DTB and the optimum cure time and scorch time of the corresponding reference mix A_1 . The addition of 2 mmol DTB reduces the optimum cure time to almost half that using MBS alone (from 16.5 to 8 min). Increasing the concentration of DTB produces a further reduction in the optimum cure time. The preferable dosage of 2 mmol DTB can activate the curing process by initiating the cure quickly and increasing the rate of cure.

The CRI is a measure of the speed with which the cure reaction is taking place. The CRI values are higher for DTB/MBS alone, which indicates faster curing. The values are higher for *o*- and *p*-DTB systems than for *m*-DTB systems, which explains the lower cure time in those vulcanizates.

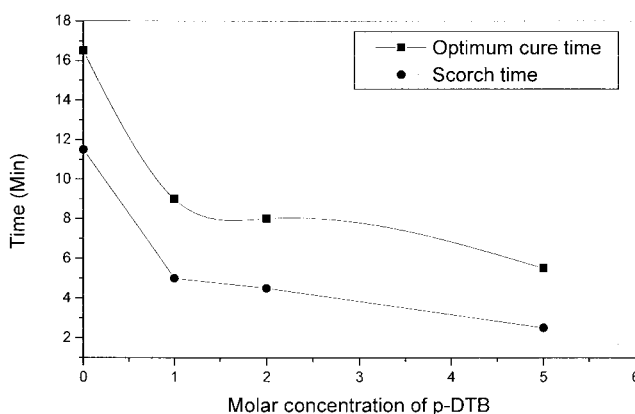
Considering the fact that practical rubber mixes can be obtained using DTB as the secondary accelerator in the sulfur vulcanization of NR, the vulcanizate properties of these mixes were investigated further. To correlate the variation in the tensile properties of various mixes before and after aging to the number of crosslinks, the total crosslink density of the different vulcanizates was also estimated.

The tensile strength values are shown in Table III. This value is the highest for the M_2 mix in which the DTB concentration is 2 mmol. With a further increase in the concentration of DTB, the tensile strength values decrease. This may be due to the desulfuration during the vulcanization process, which turns the polysulfide linkages into mono- and disulfidic links.

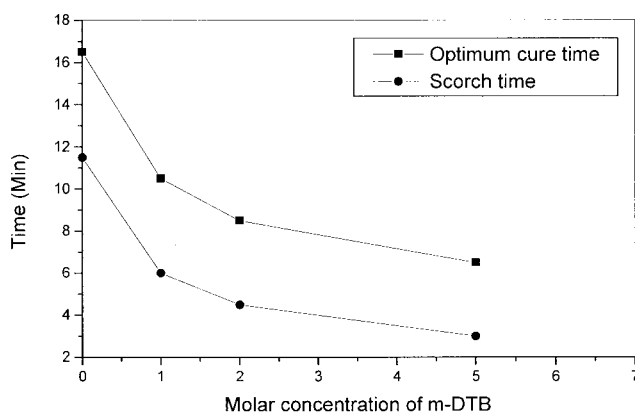
The effects of the DTB concentration on the tensile strength of the vulcanizates before and after aging is presented in Figure 8. The observed behavior is complex. For mix A_1 (i.e., without DTB), the tensile strength increases after aging. Mixes O_1 , O_3 , M_1 , M_2 , and M_3 show similar behavior (Table III). This may be due to the additional crosslinking that occurs to the vulcanizates during the aging process. Mixes O_2 , P_1 , P_2 , and P_3 present a more natural phenomenon of a reduction in the tensile strength, which is usually expected from the thermal aging process. The stress-strain curves of the different samples are given in Figure 9. All curves are typical of an elastomeric nature. It is also clear from the curves that the accelerator tolyl derivatives of DTBs do not affect the strain crys-



(a)



(b)



(c)

Figure 7 The variation in the optimum cure time and scorch time of various mixes containing (a) MBS-*o*-DTB, (b) MBS-*p*-DTB, and (c) MBS-*m*-DTB systems.

tallizing nature of NR. The 300% modulus values are also given in Table III. The highest modulus is shown by the M_2 mix, The influence of thermal aging on the 300% modulus is presented in Figure 10.

The elongation at break (Table III) decreases with an increased concentration of DTB. It can be seen that among the unaged binary systems under study, mix

TABLE III
Tensile Properties of Vulcanizates Containing MBS-DTB and MBS-DPG

Mixes	Tensile Strength (MPa)			300% Modulus (MPa)			Elongation at Break (%)		
	Before Aging	After Aging	Retention (%)	Before Aging	After Aging	Retention (%)	Before Aging	After Aging	Retention (%)
O ₁	17.2	18.3	106.39	2.6	3.2	123	942	928	98.51
O ₂	18.8	17.5	93.08	3.2	3.6	112	920	902	98.04
O ₃	18.6	19.8	106.45	4	4.5	112	930	918	98.7
P ₁	17.6	16.2	92.04	2.7	3.2	118	935	906	96.89
P ₂	19.66	17.5	89.01	4	4.2	105	905	882	97.45
P ₃	19.8	18.2	91.91	3.9	4.5	115	917	908	99.02
M ₁	17.8	20.2	113.48	3	3.8	127	920	904	98.26
M ₂	20	22.1	110.5	4.2	4.6	110	860	810	94.18
M ₃	19.7	23.1	117.25	4.15	4.7	113	876	812	92.69
A ₁	16	17.3	108.12	2.1	2.3	110	980	940	95.92
D ₁	16	13.2	82.5	2.6	2.8	108	938	888	94.67
D ₂	16.2	13.1	80.86	3.2	3	94	938	862	91.9
D ₃	16.9	13.3	78.69	3.1	3.4	110	932	841	90.23

O₁ has the highest elongation at break and mix M₂ has the lowest elongation at break. The influence of thermal aging on the elongation at break is presented in Figure 11.

Other physical properties that we investigated include the hardness (Shore A), heat buildup, resilience, tear strength, and crosslink densities. These are reported in Table IV. In the case of vulcanizates containing DTBs, the tear strength slightly increases with an increase in the dosage of DTB up to 2 mmol DTB and then decreases; while hardness and resilience remain almost constant. The optimum dosage of 2 mmol *o*- and *p*-DTB give comparable values of hardness, resilience, and tear strength to those of the reference mix whereas *m*-DTB gives higher values for the resilience and tear strength. This may be attributable to the high crosslink density in meta derivative than that of *o*- and *p*-DTB.

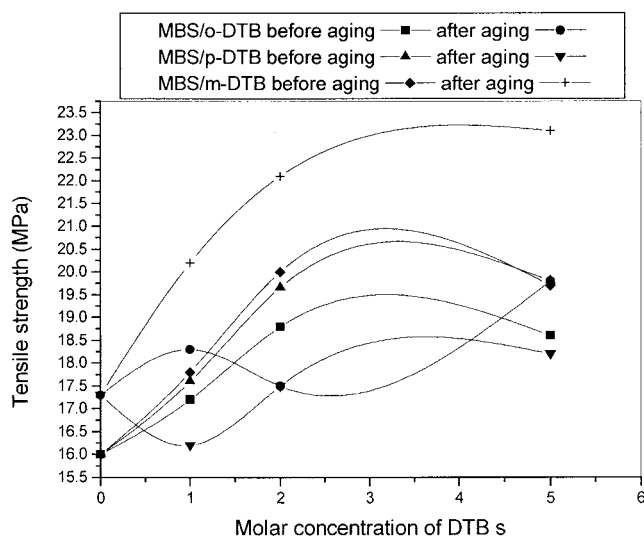


Figure 8 The variation of the tensile strength of the vulcanizates with varying concentrations of DTBs.

CONCLUSIONS

The use of DTB as a secondary accelerator for MBS was investigated emphasizing the processing characteristics and mechanical properties. We found that a

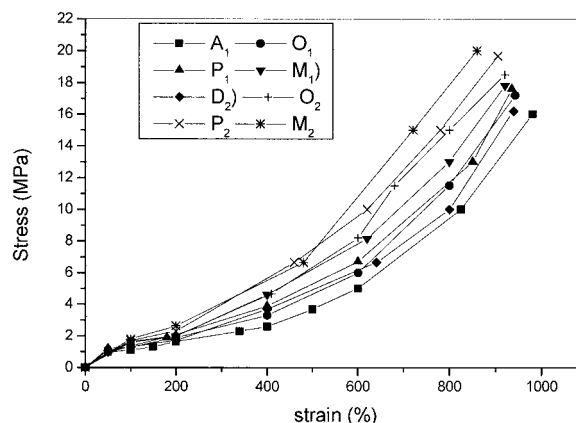


Figure 9 The stress-strain curves of MBS-DTB vulcanizates.

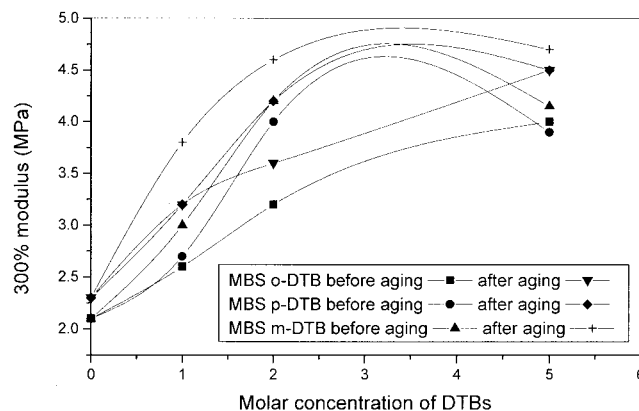


Figure 10 The effect of thermal aging on the 300% modulus of NR vulcanizates with varying concentrations of DTBs.

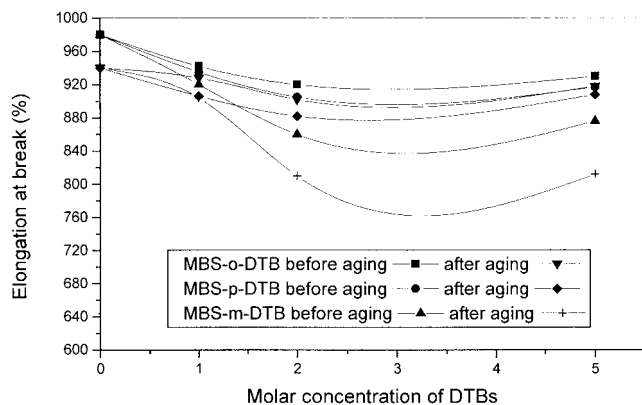


Figure 11 The effect of thermal aging on the elongation at break of NR vulcanizates with varying concentrations of DTBs.

DTB concentration of 2 mmol reduces the optimum cure time of the mixes and improves the production rate of the vulcanizates. However, the scorch time was

TABLE IV
Other Physical Properties of MBS-DTB and MBS-DPG
Vulcanizates

Mix No.	Hardness (Shore A)	Heat Buildup (°C)	Resilience (%)	Tear Strength (N/mm)	Crosslink Density (mmol/kg RH)
O ₁	24	11	66.3	27.88	27.33
O ₂	25	10	66.9	29.45	32.2
O ₃	24	10	65.7	26.79	29.73
P ₁	24	11	66.3	28.92	28.2
P ₂	25	10	67.5	29.52	34.00
P ₃	24	10	67.2	28.59	32.2
M ₁	25	11	69.1	30.26	28.48
M ₂	23	10	69	32.63	35.52
M ₃	22	11	70.1	28.53	34.2
A ₁	24	12	66.1	26.85	25.55
D ₁	28	14	62	25	25.2
D ₂	26	12	65	28.2	26.4
D ₃	25	11	67	28.4	26.7

reduced. Because *o*- and *p*-DTBs are more nucleophilic than *m*-DTB, the results clearly indicate a nucleophilic reaction mechanism in the systems under investigation. The tensile and other physical properties (hardness, heat buildup, resilience, and tear strength) of these vulcanizates were better than or comparable to those of the reference mix.

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