STUDIES ON A NEW BINARY ACCELERATOR SYSTEM FOR THE SULFUR VULCANIZATION OF STYRENE-BUTADIENE RUBBER*

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ABSTRACT

The chemical reactions involved when a binary accelerator system is used in rubber vulcanization varies with the systems used. The exact mechanism of these reactions is not fully understood even now. Accelerators in which sulfur is combined as S—S, C—S—C, or S—N are generally inactive at low vulcanization temperatures because of the high thermal stability of their sulfur bonds. But sulfur-containing nucleophiles such as thiourea or its derivatives enable accelerators like TMTD or CBS to operate at lower vulcanization temperature, indicating a nucleophilic reaction mechanism in these vulcanization reactions. But, no conclusive evidence is given for such a postulate. In the present study, 1-phenyl-2,4-dithiobiuret and 1,5-diphenyl-2,4-dithiobiuret, which are more nucleophilic than thiourea but which vary in their nucleophilic reactivity, were tried as secondary accelerators in binary systems containing TMTD or CBS in sulfur vulcanization of SBR. Both the above dithiobiurets were found to reduce the optimum cure time considerably compared to the reference mixes. 1-phenyl-2,4-dithiobiuret, which is more nucleophilic than 1,5-diphenyl-2,4-dithiobiuret, is found to reduce the optimum cure time more, showing a nucleophilic reaction mechanism in the systems under review. In both cases, the optimum dosage of the secondary accelerator required has been established. The vulcanizates obtained with these new systems showed definite increase in tensile properties and good retention of these properties after aging. In the evaluation of other physical properties, these vulcanizates gave promising results. In order to correlate these physical properties to the type of chemical crosslinks formed, chemical characterization of the vulcanizates was also carried out. Also, to study the effect of these nucleophiles on the temperature of vulcanization, these mixes were cured and evaluated at two different temperatures, *viz.*, 120°C and 150°C.

To overcome the lower green strength and gum tensile strength in SBR, incorporation of fine reinforcing fillers and the use of special combinations of accelerators is required. In this context, the study was extended to evaluate the effect of fillers—carbon black, precipitated silica, and china clay—on the cure characteristics and vulcanizate properties.

INTRODUCTION

Vulcanization of rubber using binary accelerator systems is known to give superior chemical and physical properties to the vulcanizates. The chemical reactions involved, when a binary accelerator system is used in rubber vulcanization, varies with the systems used. The exact mechanism of these reactions is not fully understood even now. Accelerators in which sulfur is combined as S—S, C—S—C, or S—N are generally inactive at lower temperature because of the high thermal stability of their sulfur bonds. In his studies on the vulcanization of natural rubber latex using TMTD–thiourea binary systems, Philpott[1] has shown that, sulfur-containing nucleophiles such as thiourea, enabled accelerators like TMTD to operate at lower vulcanization temperatures. He suggested an ionic mechanism, where the S—S bond in TMTD is cleaved by the nucleophile (Y^-) produced from thiourea,

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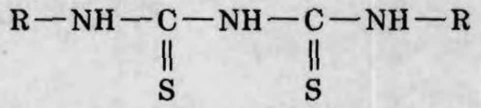
$$\mathrm{R{-}S{-}S{-}R_1 + Y^- \rightarrow RSY + R_1S^-}.$$

In the case of the sulfenamides ($\mathrm{XS{-}NR_2}$) scission at the $\mathrm{S{-}N}$ center would take place by the subsequent displacement of the nitrogen-containing anion, $\mathrm{R_2N^-}$.

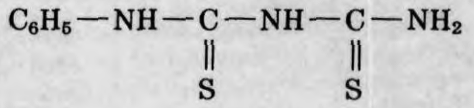
A perusal of the literature indicates that even though a number of thiourea derivatives have been tried in rubber vulcanization[2-4], the acceleration activity of dithiobiuret derivatives of thiourea have not been investigated. We undertook this study assuming that dithiobiuret derivatives of the general formula, I, which will show more nucleophilic activity than simple thiourea derivatives, will be more reactive in the rubber vulcanization reaction with accelerators of the thiuram or sulfenamide type:



$$\mathrm{R{-}NH{-}\underset{\underset{S}{\|}}{C}{-}NH{-}\underset{\underset{S}{\|}}{C}{-}NH{-}R}$$

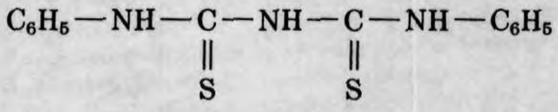
I

Even though suggestions have been made for the nucleophilic reactivity of thiourea and its derivatives in binary systems containing these compounds, no conclusive proof for such a postulate was given in the earlier work. Therefore, one of the aims of this study was to give additional proof of the theory of nucleophilic reactivity in such binary systems. To accomplish this, we synthesized two dithiobiurets of differing nucleophilic reactivity and studied their behavior as coaccelerators. The two compounds shown below were synthesized according to Joshua *et al.*[5]



$$\mathrm{C_6H_5{-}NH{-}\underset{\underset{S}{\|}}{C}{-}NH{-}\underset{\underset{S}{\|}}{C}{-}NH_2}$$

DTB-II



$$\mathrm{C_6H_5{-}NH{-}\underset{\underset{S}{\|}}{C}{-}NH{-}\underset{\underset{S}{\|}}{C}{-}NH{-}C_6H_5}$$

DTB-III

In this study, we evaluated DTB-II and DTB-III in binary accelerator systems with TMTD or CBS for sulfur vulcanization of styrene–butadiene rubber (SBR-1502) using standard compounding recipes. In all the systems studied, it was found that the dithiobiurets act as better nucleophiles, as evidenced by the significant reduction in cure time in the compounds containing DTB-II and DTB-III, compared to the reference mixes. Also it was found that the reduction in cure time is greater in systems containing the more nucleophilic DTB-II than in those containing DTB-III. These facts support the nucleophilic attack concept of accelerated vulcanization in the systems under review.

Moreover, these vulcanizates showed a definite increase in tensile properties and good retension of these properties after heat aging in air. Other physical properties of these vulcanizates were also promising. In view of this significant reduction in cure time along with the increase in tensile properties of the vulcanizates containing dithiobiurets, we made a thorough study of these systems with regard to the cure characteristics of the mixes, physical properties of the vulcanizates, and types of crosslink formation. Also, to evaluate the vulcanization temperature sensitivity of these nucleophiles, mixes were cured at two different temperatures, *viz.*, 120° and 150°C.

Since SBR does not stress crystallize, green strength and tensile properties are poor in gum vulcanizates. Thus, fine reinforcing fillers are required to achieve useable properties. To address this issue, we extended the study to include various fillers in the TMTD–dithiobiuret binary systems. For this aspect of the work, compounds and vulcanizates were prepared with 50 phr carbon black (HAF), 50 phr precipitated silica, and 50 phr china clay.

EXPERIMENTAL

DITHIOBIURET SYNTHESIS

1-Phenyl-2,4-dithiobiuret[5] *(DTB-II).*—Ammonium phenyl dithiocarbamate was first prepared by the reaction of carbon disulfide and aniline in ammoniacal medium at 0°C. The former was steam distilled in the presence of lead nitrate to obtain phenyl isothiocyanate. The latter (0.025 mol) was added dropwise to a stirred solution of thiourea (0.025 mol) and powdered sodium hydroxide (0.025 mol) in acetonitrile (15 mL) and the reaction mixture was heated at 60°C for $\frac{1}{2}$ h, when a clear solution resulted. This was then diluted with water (150 mL), filtered, and the filtrate acidified with concentrated hydrochloric acid (4 mL, 33%). The crude 1-phenyl 2,4-dithiobiuret obtained was dissolved in a minimum quantity of 4% aqueous sodium hydroxide to remove any unreacted thiourea and filtered. The alkaline filtrate, on acidification at 0°C, afforded 1-phenyl-2,4-dithiobiuret, which after recrystallization from ethanol, had a melting point of 180°C.

1,5-Diphenyl-2,4-dithiobiuret[5] *(DTB-III).*—Phenyl thiourea was prepared by the reaction of aniline with ammonium thiocyanate in hydrochloric acid. Phenyl isothiocyanate prepared as detailed in the above section (0.025 mol) was added dropwise during 5 min to a stirred solution of phenyl thiourea (0.025 mol) and powdered sodium hydroxide (0.025 mol) in acetonitrile (15 mL). The reaction mixture was heated to 60°C and stirred at this temperature for $\frac{1}{2}$ h when a clear solution resulted. This was diluted with water (150 mL) and filtered. The filtrate was acidified with concentrated hydrochloric acid (4 mL, 33%) and the precipitated product was collected and redissolved in a minimum quantity of 4% aqueous sodium hydroxide to remove any unreacted phenyl thiourea. This solution was filtered and the alkaline filtrate was acidified with hydrochloric acid at 0°C, affording 1,5-diphenyl-2,4-dithiobiuret, which after recrystallization from ethanol had a melting point of 143°C.

COMPOUNDING AND TESTING

Styrene–butadiene rubber used in the experiment was Synaprene 1502 obtained from Synthetics and Chemicals, Ltd. The raw polymer had a Mooney viscosity, *ML* 1 + 4 (100°C), of 52.0. The other compounding ingredients were as follows: zinc oxide, 98% purity supplied by Meta Zinc, Ltd., Bombay, India; stearic acid, rubber grade, supplied by Rubochem Industries; CBS (Santocure CBS), 99% purity, supplied by Polyolefin Industries; sulfur, 98% soluble in CS_2, supplied by Standard Chemicals Co., Pvt., Ltd.; thiourea, analytical grade (99.5% purity), supplied by Sisco Research Laboratories; propane-2-thiol, 1-hexanethiol, and piperidine, analytical grade, supplied by Fluka, Germany.

The SBR gum formulations, given in Tables I and II, were evaluated to determine the optimum concentration of the dithiobiuret with TMTD and CBS, respectively, in the vulcanization reaction under standard conditions. Compounds A_0, containing TMTD alone, and B_0,

TABLE I

FORMULATION OF THE MIXES CONTAINING TMTD–DITHIOBIURET

Ingredients	A_0	B_0	A_1	A_2	A_3	A_4	A_5	B_1	B_2	B_3	B_4	B_5
SBR 1502	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2
TMTD	1.5	1.5		1.5	1.5	1.5	1.5		1.5	1.5	1.5	1.5
Thiourea	—	0.5	—	—	—	—	—	—	—	—	—	—
DTB-II	—	—	0.5	1.5	1.0	0.5	0.25	—	—	—	—	—
DTB-III	—	—	—	—	—	—	—	0.5	1.5	1.0	0.5	0.25
Sulfur	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

FORMULATION OF THE MIXES CONTAINING CBS–DITHIOBIURET

Ingredients	C_0	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4
SBR 1502	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2
DTB-II	—	1.5	1.0	0.5	0.25	—	—	—	—
DTB-III	—	—	—	—	—	1.5	1.0	0.5	0.25
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

containing TMTD with 0.5 phr thiourea, are reference mixes. Compounds A_2–A_5 contain different concentrations of DTB-II ranging from 1.5 phr to 0.25 phr with 1.5 phr TMTD. Compounds B_2–B_5 contain different concentrations of DTB-III ranging from 1.5 phr to 0.25 phr with 1.5 phr TMTD. Compound C_0 contains CBS alone, whereas compounds C_1–C_4 contain different concentrations of DTB-II ranging from 1.5 phr to 0.25 phr with 1.5 phr CBS. Compounds D_1–D_4 contain different concentrations of DTB-III ranging from 1.5 phr to 0.25 phr with 1.5 phr CBS. Trial compounds were also prepared without TMTD or CBS (mixes A_1 and B_1) but they cured very very slowly and hence were not evaluated further.

The filled formulations studied are described in Table III. These were limited to the optimum dosage TMTD–dithiobiuret systems and reference compounds.

The optimum cure time for the various mixes at 150°C and at 120°C were evaluated using a Monsanto Rheometer (R-100) according to ASTM Standard D 2084-88. The scorch time of the mixes at 120°C was evaluated using a Mooney Viscometer (ASTM D 1646-89). In running the scorch test, the sample was allowed to warm up for one minute after the platens were closed, prior to starting the motor. The time for a 5 unit rise above the minimum is taken as the Mooney Scorch Time, t_5.

The cure characteristics of these gum formulations are given in Tables IV and V. The cure rate index, determined from the rheographs of the respective compounds, is reported as, $100/(t_{90} - t_2)$, where t_{90} and t_2 are the times corresponding to the optimum cure and two units above minimum torque, respectively. The induction time, t_1 is the time for one unit (0.1 Nm) rise above the minimum torque (about 5% vulcanization). Optimum cure time, t_{90}, is the time to 90% of the maximum torque.

TABLE III

FORMULATION OF MIXES CONTAINING FILLERS

Ingredients	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
SBR 1502	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2
HAF black	50	50	50	50	—	—	—	—	—	—	—	—
Precipitated silica	—	—	—	—	50	50	50	50	—	—	—	—
China clay	—	—	—	—	—	—	—	—	50	50	50	50
Naphthenic oil	5	5	5	5	5	5	5	5	5	5	5	5
TMTD	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Thiourea	—	0.5	—	—	—	0.5	—	—	—	0.5	—	—
DTB-II	—	—	0.5		—	—	0.5	—	—	—	0.5	—
DTB-III	—	—		0.5	—	—	—	0.5	—	—	—	0.5
Sulfur	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 IV

CURE CHARACTERISTICS OF THE MIXES CONTAINING TMTD-DITHIOBIURETS

	Mix no., cured at 150°C										Mix no., cured at 120°C					
	A_0	B_0	A_2	A_3	A_4	A_5	B_2	B_3	B_4	$B_{5'}$	A_0	B_0	A_2	A_3	B_2	B_3
Min. torque, dN·m	10.5	11.0	14.0	13.0	10.5	10.0	13.0	11.0	11.0	10.5	15.0	15.0	16.0	16.0	19.0	15.0
Max. torque, dN·m	65.0	56.0	61.0	63.0	61.5	65.0	65.0	64.0	66.0	66.0	55.0	56.0	58.0	58.0	55.0	57.0
Induction time, t_1, min	3.0	2.0	0.5	0.75	2.0	2.5	1.5	2.0	2.0	2.5	15.0	11.0	2.5	6.0	1.5	7.0
Scorch time, min	3.5^a	2.5^a	1.0^a	1.25^a	2.5^a	3.0^a	2.0^a	2.5^a	2.5^a	3.0^a	17^b	13^b	3.0^b	7.5^b	2.0^b	9.0^b
Optimum cure time, t_{90}, min	18.5	11.5	9.5	11.5	12.5	15.5	15.5	17.5	18.0	18.5	70.0	64	42	63	55.5	77.5
Cure-rate index	6.67	11.1	11.1	9.76	10.0	8.0	6.78	6.67	6.45	6.45	1.89	1.96	2.56	1.80	1.87	1.96

[a] Rheometer scorch time (t_2).

[b] Mooney Scorch time (t_5).

TABLE V

CURE CHARACTERISTICS OF THE MIXES CONTAINING CBS–DITHIOBIURETS

	Mix no., cured at 150°C									Mix no., cured at 120°C			
	C_0	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4	C_1	C_2	D_1	D_2
Min. torque, dN·m	10.0	11.0	10.0	10.0	10.0	10.0	10.0	11.0	10.5	14.5	15.0	16.0	9.0
Max. torque, dN·m	37.0	44.0	44.0	45.0	42.0	44.0	46.5	47.0	40.0	45.0	46.0	47.0	45.0
Induction time, t_1, min	16.0	1.5	2.0	4.0	7.0	2.5	4.0	9.0	9.0	4.5	6.0	10.0	18.0
Scorch time, min	17.5[a]	2.0[a]	2.5[a]	5.0[a]	8.5[a]	3.0[a]	5.0[a]	10.5[a]	11.5[a]	6.0[b]	7.0[b]	13.0[b]	22.0[b]
Optimum cure time, t_{90}, min	47.5	19.0	25.5	28.0	32.0	22.5	29.5	38.5	45.0	62.0	95.0	68.5	119
Cure-rate index	3.30	5.88	4.35	4.33	4.25	5.13	4.08	3.57	2.99	1.80	1.14	1.79	1.03

[a] Rheometer scorch time (t_2).

[b] Mooney scorch time (t_5).

All compounds were prepared on a laboratory size two-roll mixing mill (30 × 15 cm) at a friction ratio of 1 : 1.25, according to the procedure given in ASTM D 3185-88. Test specimen vulcanization was carried out in 18″ (460 mm) × 18″ (460 mm) platens using a steam heated press maintained at 150°C, 45 kg/cm^2 pressure. Tensile properties were determined according to ASTM Standard D 412-87 with dumbbell specimens in a Zwick Universal Testing Machine at a pulling rate of 500 mm per min at room temperature (30°C). Tear resistance was determined by ASTM Method D 624-86 using unnicked 90° angle test pieces.

Hardness was measured according to ASTM D 2240-86, and compression set according to ASTM D 395-89 (Method B). For determination of rebound (resilience) a Dunlop Tripsometer (British Standard 903, pt. 22, 1950) was used at a temperature of 35°C. Heat build-up was measured using a Goodrich Flexometer following ASTM standard D 623-88 at a temperature of 50°C; stroke, 4.45 mm; and load, 10.9 kg. Aging was carried out at 70°C for 96 h in a tubular aging oven according to ASTM D 865-88.

DETERMINATION OF CONCENTRATION OF CHEMICAL CROSSLINKS[6,7]

Vulcanizate samples weighing 0.2–0.3 g were allowed to stand in benzene containing 0.1% phenyl-β-naphthylamine (PBN). After 24 h, the samples were transferred to pure benzene for an additional 2 h. From the values of the original test specimen mass (a_1), swollen specimen mass (a_2), and mass of the specimen after drying for 6 days at laboratory temperature (a_3), the volume fraction of rubber in the swollen network (V_r) was calculated as follows[8]:

$$V_r = \frac{(a_3 - a_1 \cdot S_1/S_2) \cdot 1/d_r}{(a_3 - a_1 \cdot S_1/S_2) \cdot 1/d_r + (a_2 - a_3) \cdot 1/d_b}; \tag{1}$$

where, S_1 = the sum of the contents of sulfur and zinc oxide (phr), S_2 = the sum of the contents of all the components in the mix including rubber (phr), d_r = density of rubber 0.940 g/cm^3 for SBR, and d_b = density of benzene, 0.865 g/cm^3. From the value of V_r so obtained, the elastic constant, C_1, was calculated using the equation[9,10],

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = \frac{2C_1 V_s (V_r^{1/3} - V_r/2)}{RT}, \tag{2}$$

where χ is a parameter characteristic of interaction between the rubber network and the swelling agent. For the SBR–benzene system, the value of χ could be calculated from the relationship[11],

$$\chi = 0.330 + 0.43V_r. \qquad (3)$$

In Equation (2), V_s is the molar volume of benzene (90 cm^3/mol), R the gas constant, and T the absolute temperature. The C_1 value so obtained was converted into the concentration of chemical crosslinks, $(2\,M_{c,chem})^{-1}$, using the Mullins formula[12].

$$C_1 = [\rho RT(2\,M_{c,chem})^{-1} + 0.78 \times 10^5][1 - 2.3\,M_{c,chem}\,\bar{M}_n^{-1}], \quad \text{Pa}, \qquad (4)$$

where ρ is the density of the rubber network, and $\bar{M}_n$ is the number-average molecular weight of the rubber before vulcanization. In the case of vulcanizates containing HAF black, the values of V_r, obtained as above, were converted into V_{ro} (the value V_r would have had in the absence of the black) by means of the following equation[8,13]:

$$V_{ro}/V_r = 0.56[\exp(-z)] + 0.44, \qquad (5)$$

where z is the weight fraction of carbon black in the vulcanizate. V_{r^o} was then substituted in Equation (2) in place of V_r to obtain the crosslink density.

DETERMINATION OF CONCENTRATION OF CROSSLINKS AFTER CLEAVAGE OF POLYSULFIDIC CROSSLINKS

A test specimen weighing about 0.2–0.3 g (a_1) was allowed to stand in an excess of benzene containing 0.1% PBN for 24 h at 28°C. Then the solvent was replaced by 0.4 M solution of propane-2-thiol and piperidine in benzene containing 0.5% PBN and allowed to stand for 2 h. On completion of the reaction, the sample was removed from the reagent solution, washed with petroleum ether (b.p. 40°–60°C) four times, surface dried on filter paper as quickly as possible, and dried in a vacuum to constant weight at room temperature. The specimen was then swollen in benzene containing 0.1% PBN for 24 h. Finally, the vulcanizate was extracted for 2 h in pure benzene and weighed (a_2). The mass of the dried test specimen (a_3) was determined after drying for 6 days at laboratory temperature. From the values a_1, a_2, and a_3, V_r was calculated as before, and the concentration of chemical crosslinks after cleavage was determined.

TABLE VI

CURE CHARACTERISTICS OF THE MIXES CONTAINING FILLERS

Mix no.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Min. torque, dN·m	17.5	18.0	18.0	18.0	18	18	18.5	18.0	19	20	20	20
Max. torque, dN·m	90	85	93	90	66	63	67	66	64	65	59	54
Induction time, t_1, min	2.0	2.0	1.0	2.0	1.5	1.5	1.25	1.25	1.5	1.25	1.5	1.5
Rheometer scorch time t_2, min	2.5	2.25	1.5	2.25	1.75	1.75	1.5	1.5	1.75	1.5	1.75	1.75
Optimum cure time t_{90}, min	13.0	12.0	10.0	11.5	12.5	11.5	11.0	11.5	10.5	9.5	12.5	13.5
Cure-rate index	9.52	10.0	11.76	8.89	9.30	10.26	10.0	10.53	11.43	12.5	9.30	8.51

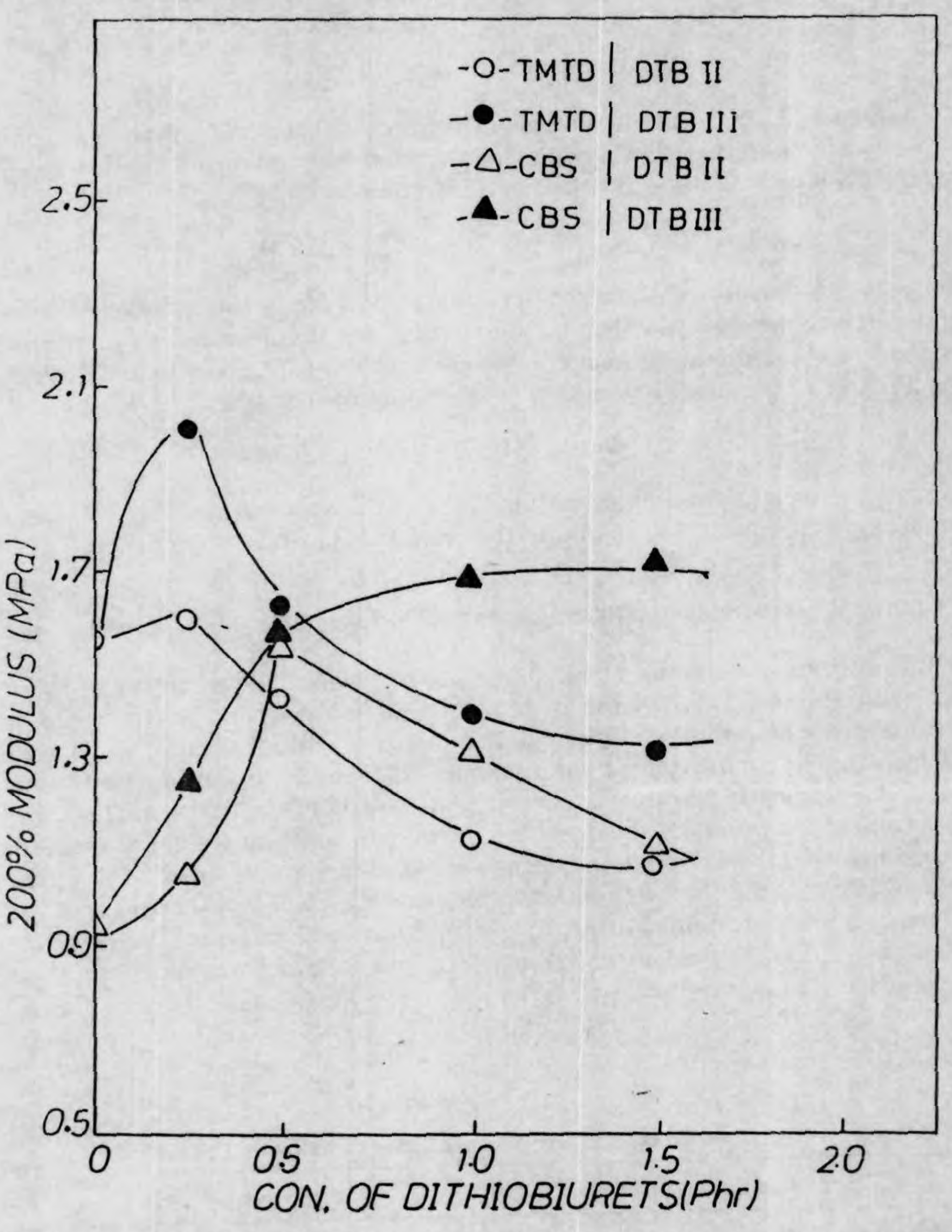


FIG. 1.—Variation of 200% modulus of vulcanizates (cured at 150°C) with concentration of dithiobiurets.

DETERMINATION OF CONCENTRATION OF CROSSLINKS AFTER THE CLEAVAGE OF POLYSULFIDIC AND DISULFIDIC CROSSLINKS

A test specimen weighing about 0.2–0.3 g (a_1) was allowed to stand in 100 mL of 1-hexanethiol in piperidine (1 M solution) containing 0.5% PBN at 28°C for 48 h with occasional agitation. On completion of the reaction, the sample was removed from the reagent solution and treated precisely as described for polysulfide cleavage. The remaining concentration of chemical crosslinks was determined from a_1, a_2, and a_3 as before.

DETERMINATION OF AMOUNT OF FREE SULFUR AND SULFIDE SULFUR

Free sulfur was determined iodometrically by converting it to sodium thiosulphate according to ASTM D 297-72. Sulfide sulfur was determined iodometrically by the formation of cadmium sulfide as described in British Standard 902, pt 1310, 1958.

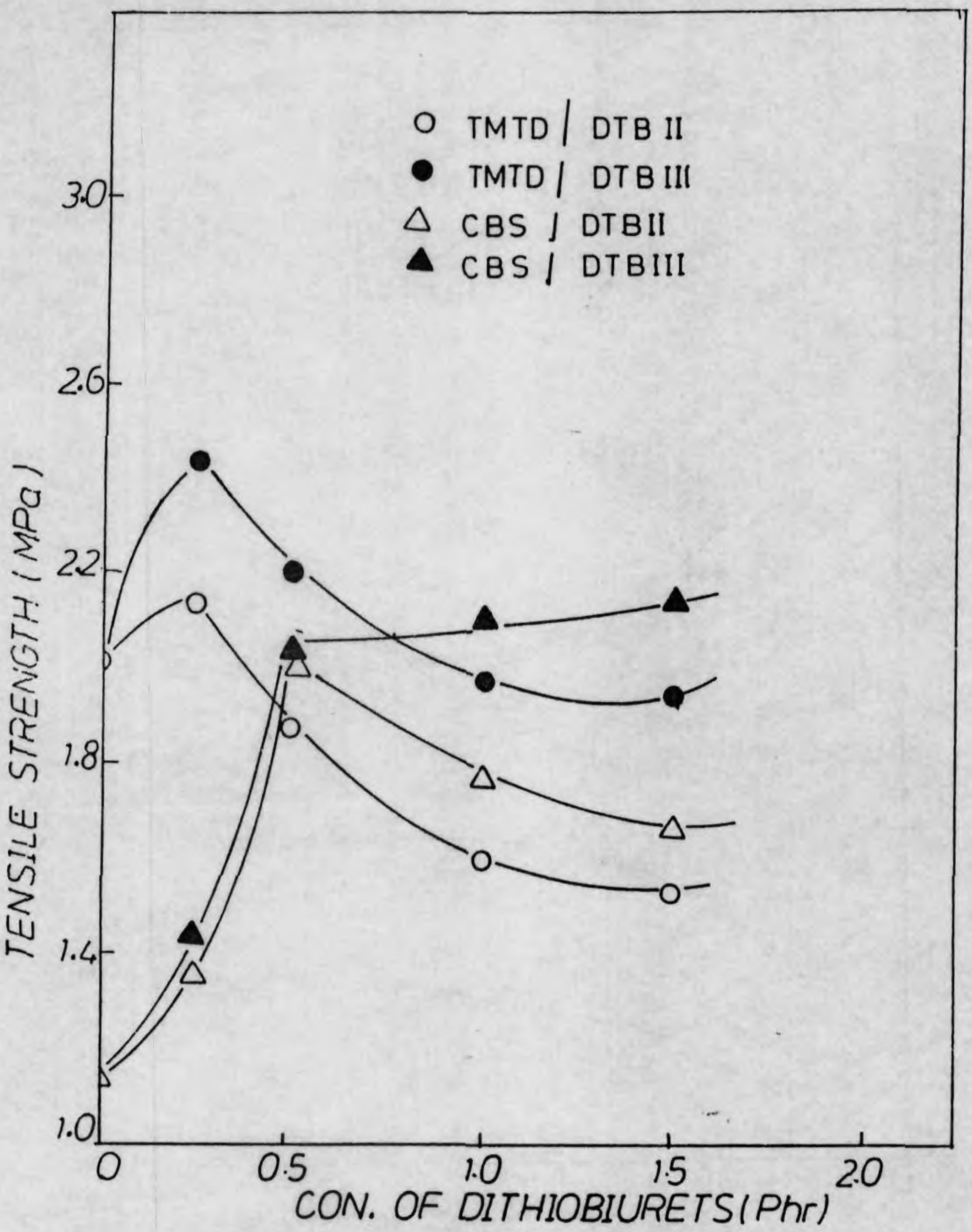


FIG. 2.—Variation of tensile strength of vulcanizates (cured at 150°C) with concentration of dithiobiurets.

RESULTS AND DISCUSSION

CURE CHARACTERISTICS

The results clearly indicate the acceleration effect of the dithiobiurets in the vulcanization systems of SBR under study. Of the two dithiobiurets studied (see Tables IV & V), the vulcanization system containing TMTD and DTB-II is found to be more effective. The results are indicative of a nucleophilic-reaction mechanism in these systems for sulfur vulcanization of SBR. The addition of 1.5 phr of DTB-II reduces the optimum cure time to almost half, and the cure rate is almost doubled. However, the very low scorch time of this mix (compound A_2) is likely to cause processing problems. Also as the concentration of dithiobiuret increases, there is an appreciable reduction in the maximum torque value of the vulcanizates.

By reducing the amount of DTB-II to 0.5 phr, a practical and optimum cure system has been obtained. At this level, there is appreciable reduction in cure time, yet scorch time and

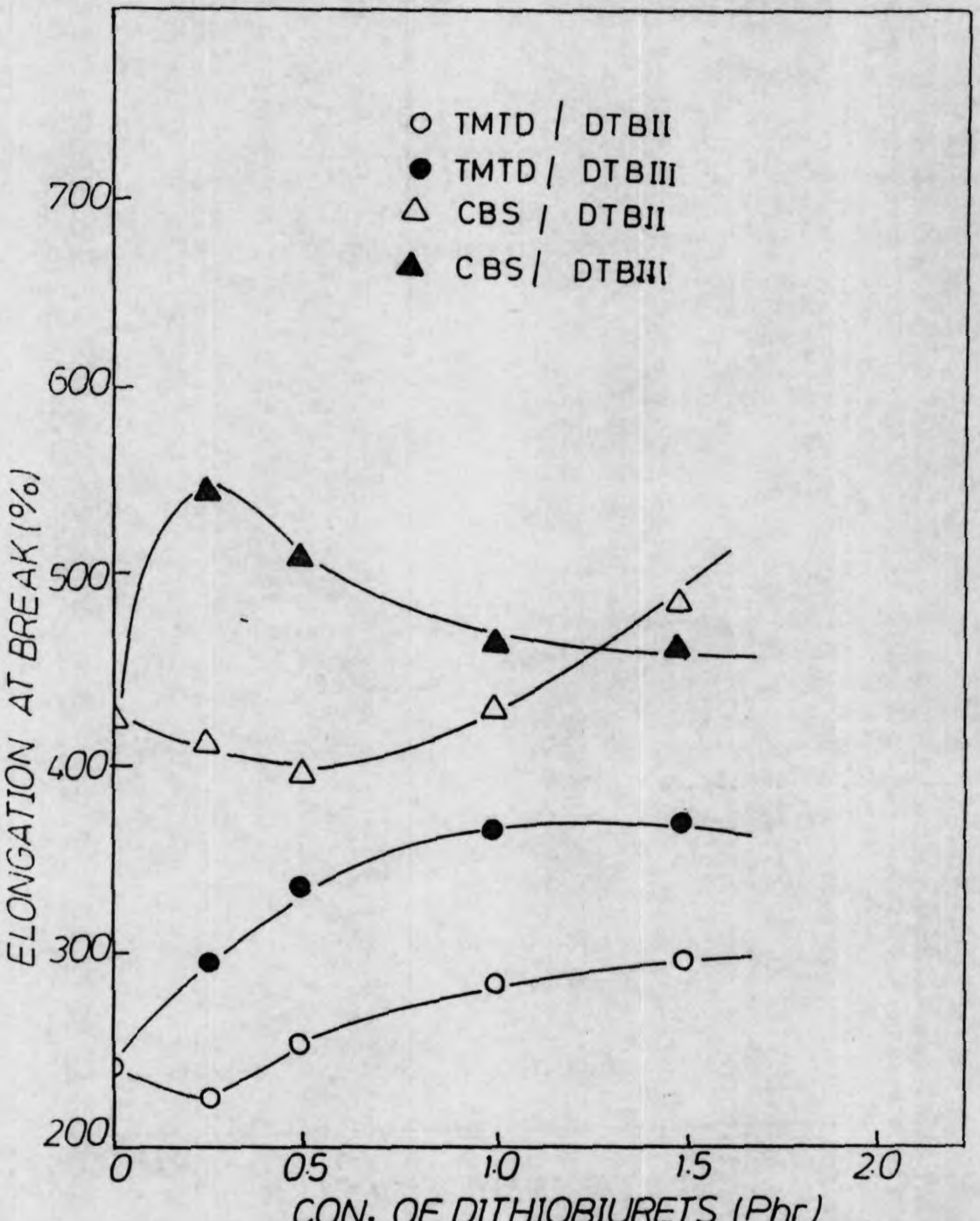


FIG. 3.—Variation of elongation at break of the vulcanizates (cured at 150°C) with concentration of dithiobiurets.

the maximum torque developed are only slightly reduced. Compared to DTB-II, DTB-III is found to be less active with TMTD. Although there is some reduction in optimum cure time and a corresponding increase in cure rate, the effects of DBT-III are less significant at the 0.5 phr dosage. Thus, 1.0 phr DTB-III is found to give optimum cure characteristics.

To see the stability of these systems at higher temperatures, reversion studies were also carried out at 170°C. Since there was no rheometer torque loss in 5 min at 170°C, these systems showed very good reversion resistance. In fact, for a long time period, the cure curve showed a plateau at 170°C. At the lower temperature, 120°C, both DTB-II and DTB-III showed a reduction in optimum cure time compared to TMTD alone or TMTD and thiourea. However, the cure rate is not appreciably increased as indicated by the cure-rate index. So the cure characteristics of the systems containing lower concentration of dithiobiurets were not further studied at 120°C.

The effect of DTB-II is found to be more pronounced in the CBS–sulfur system. Here also, the optimum dosage is found to be 0.5 phr. At this level, the optimum cure time is reduced to 28 min from 47.5 min, while the scorch time and the maximum torque developed are maintained in the desirable range. In this system also, DTB-III is found to be less active than DTB-II. However, the effect of DTB-III is more significant with CBS than in the corresponding TMTD system. It was also found that in the CBS system, a dosage of 1.0 phr DTB-III is required to get almost the same effect obtained with 0.5 phr DTB-II. Here also there is no torque loss in 5 min at 170°C, thus again showing good reversion resistance. The cure characteristics at 120°C of the reference formulation, containing CBS alone as accelerator (mix C_0), was not further studied since the scorch time was so long.

It can be seen in Table VI that the DTB-II and DTB-III systems containing HAF black show a reduction in the optimum cure time, as was the case with gum vulcanizates. DTB-II is again more active than DTB-III in this regard. In the case of the systems containing precipitated silica and china clay, dithiobiurets do not reduce the cure time considerably. This may be attributed to their highly adsorptive nature. Consequently, these nonblack filled systems were not further investigated.

TENSILE AND OTHER PHYSICAL PROPERTIES

SBR is a nonstrain crystallizing rubber and, hence, has poor gum strength. However, the new accelerators DTB-II and DTB-III are found to improve many of the tensile properties of the vulcanizates of both the TMTD and CBS systems. The effect of dithiobiuret concentration on tensile properties is shown graphically in Figures 1–3. In the case of the TMTD-dithiobiuret binary systems, 200% modulus and tensile strength improve at the lower dithiobiuret dosages increments. At the optimum dosage of 0.5 phr DTB-II and 1 phr DTB-III, there is appreciable increase in the tensile properties compared to vulcanizates containing the TMTD–thiourea accelerator system. This is also evidenced by the increase in polysulfidic linkages, shown

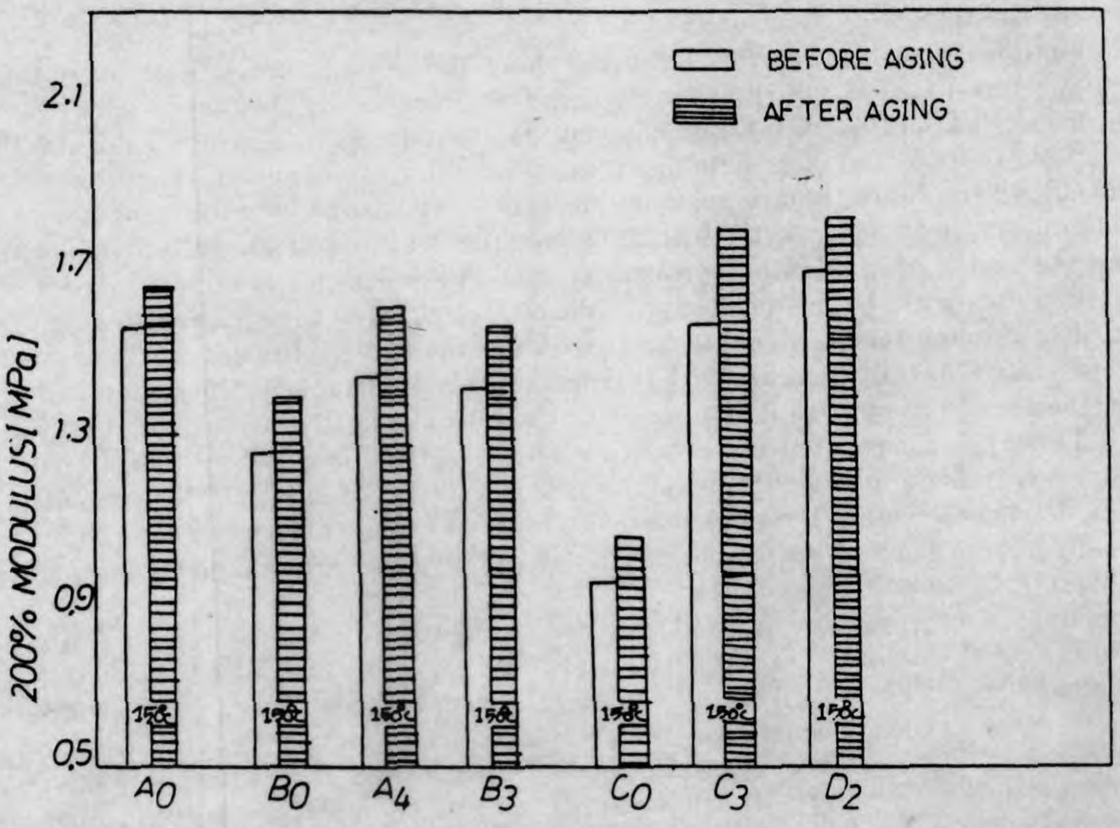


FIG. 4.—200% modulus of the vulcanizates containing optimum concentration of dithiobiurets in TMTD and CBS systems. (See Tables I and II for formulations.)

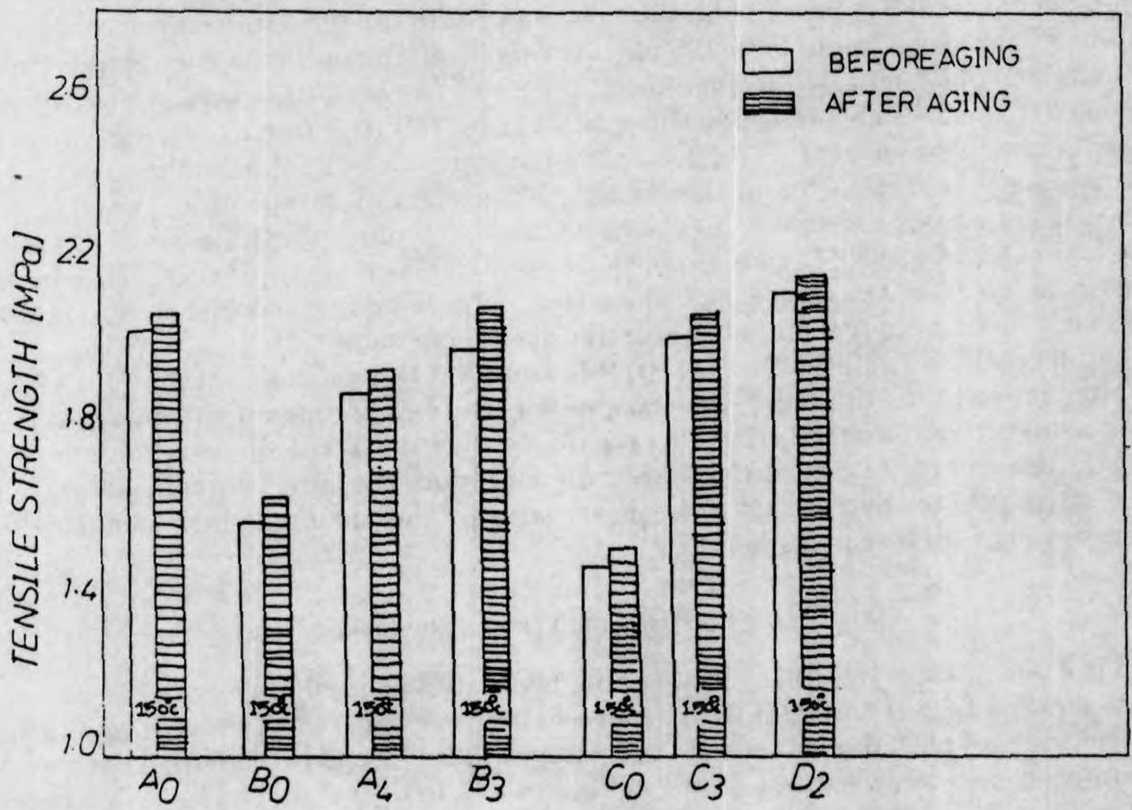


FIG. 5.—Tensile strength of vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems. (See Tables I and II for formulations.)

later in Table X. The total crosslink density and polysulfidic linkages are higher for vulcanizates containing DTB-III than those of DTB-II. This may be the reason for the higher tensile properties of the DTB-III vulcanizates.

The retention of tensile properties, following aging for the single accelerator and optimum dosage binary formulations, are shown in Figures 4–6. As expected, the percentage retention of these properties is also quite high. This can be attributed to the presence of a higher concentration of mono- and di-sulfidic linkages in the binary systems under review.

In the CBS–dithiobiuret binary systems, there is a slight change in the behavior of the two dithiobiurets. In the case of DTB-II, 200% modulus and tensile strength first increases then decreases as the coaccelerator level is increased. The elongation at break first decreases and then increases with increasing dosage of the dithiobiuret. At the optimum dosage of 0.5 phr DTB-II, maximum tensile strength and modulus is observed. In contrast, both tensile strength and modulus only increase with increasing DTB-III dosage. At the optimum dosage of 1 phr, the tensile properties are superior to those of the system containing CBS alone. Overall, DTB-III gives better tensile properties than DTB-II. This may be a reflection of the higher concentration of polysulfidic crosslinks in the system containing DTB-III, shown later in Table X. In these systems, the percentage retention of tensile properties after aging (see Figures 4–6) are quite high. This may be attributed to the presence of a higher concentration of mono- and di-sulfidic linkages.

Other physical properties of the vulcanizates studied were hardness, compression set, heat build-up, resilience, and tear strength. These data are given in Tables VII & VIII. In the case of vulcanizates containing TMTD-dithiobiuret, hardness, resilience, and tear strength generally increase as the concentration of dithiobiuret decreases, whereas compression set and heat build-up decrease over this same concentration range. At the optimum dosage of 0.5 phr DTB-II and 1.0 phr DTB-III, these properties also show improvement compared to that of the TMTD–thiourea system. This may be attributed to the fact that the total crosslink density and the number of polysulfidic linkages is greater in the TMTD–dithiobiuret vul-

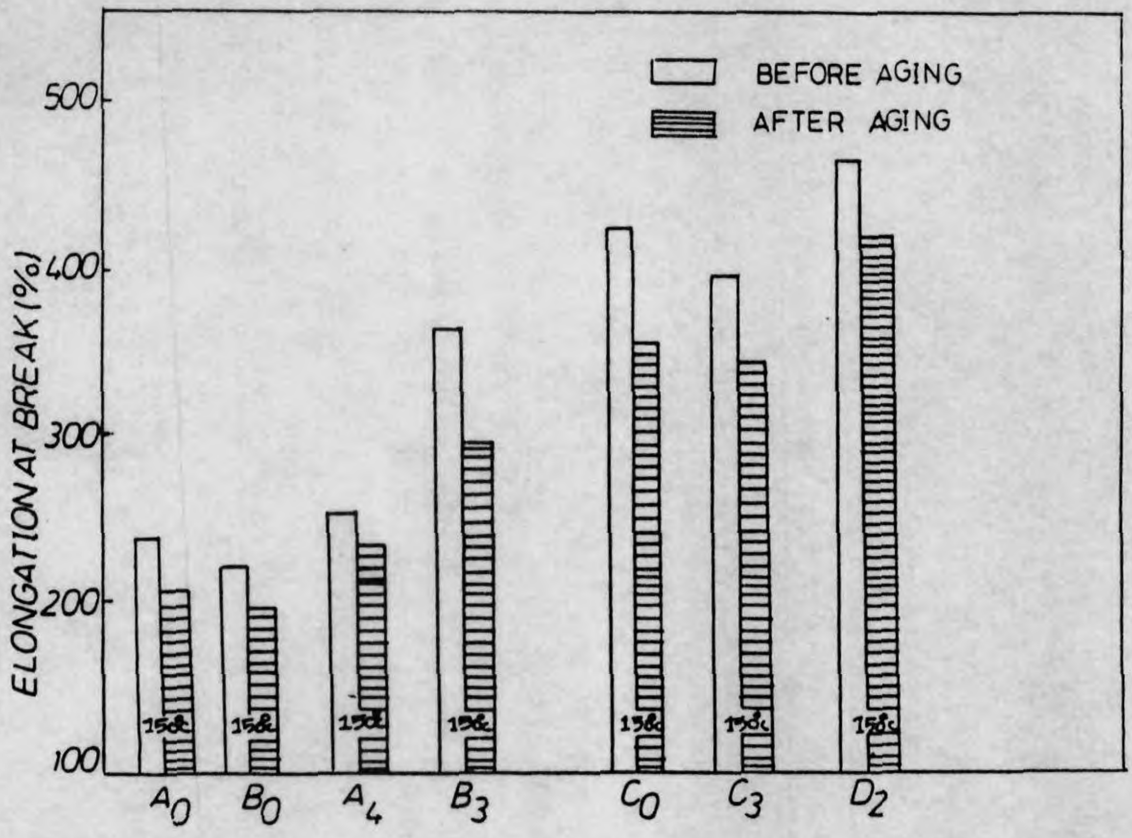


FIG. 6.—Elongation at break of vulcanizates containing optimum concentrations of dithiobiurets in TMTD and CBS systems. (See Tables I and II for formulations.)

canizates shown later in Table X. This is also consistent with the tensile-property results. Vulcanizates cured at 120°C, show lower hardness, tear strength, and resilience, but higher compression set and heat build-up, compared to those cured at 150°C. Here also, the values show a better trend than those from the TMTD–thiourea system. Within these physical property variations, DTB-III gives better values than DTB-II.

In the CBS–dithiobiuret systems, hardness, resilience, and tear strength reach a maximum with decrease in concentration of dithiobiuret; whereas compression set and heat build-up reach a minimum value then increase over the same concentration range. At the optimum levels, these properties are quite favorable compared to the reference mixes. The changes in these properties can be correlated to the total crosslink density and the polysulfidic linkages formed.

Table IX shows the physical properties of the vulcanizates containing HAF black. The tensile properties of the vulcanizates containing dithiobiurets are higher than those containing TMTD alone and TMTD–thiourea. Other physical property values are comparable to those of TMTD alone and the TMTD–thiourea systems.

CHEMICAL CHARACTERIZATIONS

The total chemical crosslink density and crosslink type distribution (mono-, di-, and polysulfidic linkages), free sulfur, and zinc-sulfide sulfur were evaluated on vulcanizates from TMTD alone, CBS alone, TMTD–thiourea, and the optimum dosage dithiobiuret binary systems. The results are given in Table X. The total crosslink density and polysulfidic linkages of the TMTD–DTB-II vulcanizate cured at 150°C are slightly less than the TMTD vulcanizate, but higher than the TMTD–thiourea vulcanizate. The DTB-III binary system gives the highest values of total crosslink density and polysulfidic linkages. As mentioned earlier, these systems show better modulus, tensile strength, hardness, and resilience values than those of DTB-II.

TABLE VII

PHYSICAL PROPERTIES OF VULCANIZATES CONTAINING TMTD-DITHIOBIURET

	Mix no., cured at 150°C										Mix no., cured at 120°C					
	A_0	B_0	A_2	A_3	A_4	A_5	B_2	B_3	B_4	B_5	A_0	B_0	A_2	A_3	B_2	B_3
Hardness, Shore A	43	32	38	41	43	45	40	42	44	46	29	30	32	32	31	32
Compression set, %	15.05	19.20	17.40	16.70	15.25	14.80	16.80	15.53	14.90	14.43	28.35	22.10	18.75	17.90	20.25	19.40
Heat build-up, ΔT°C	15	26	22	20	19	17	24	22	19	18	15	24	20	18	22	20
Resilience, %	65.50	63.90	63.47	64.15	65.85	66.50	64.15	65.68	66.90	14.41	50.15	51.30	60.38	62.70	63.40	63.90
Tear strength, kN/m	14.06	12.68	10.46	11.55	12.53	14.15	11.85	12.59	14.41	14.85	10.25	11.40	11.86	11.90	10.30	12.32

TABLE VIII

PHYSICAL PROPERTIES OF THE VULCANIZATES CONTAINING CBS-DITHIOBIURET

	Mix no., cured at 150°C									Mix no., cured at 120°C			
	C_0	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4	C_1	C_2	C_3	C_4
Hardness, Shore A	34	43	45	45	40	48	46	44	35	35	36	36	38
Compression set, %	51.12	26.12	25.3	24.9	34.3	27.9	35.69	41.38	44.12	38.60	36.20	34.50	32.25
Heat build-up, ΔT°C	37	34	30	30	33	32	28	29	31	32	31	30	26
Resilience, %	46.94	53.81	55.41	55.77	50.63	63.13	61.08	60.63	54.2	51.70	53.40	49.58	61.40
Tear strength, kN/m	10.72	12.59	14.41	14.85	11.85	19.87	16.91	10.78	10.28	10.30	12.35	12.50	14.20

The larger amount of monosulfide linkages in the systems containing dithiobiurets explain their better aging properties. The lower free-sulfur concentration for dithiobiuret systems, suggests more efficient utilization of sulfur. The higher zinc-sulfide sulfur concentration in the binary systems is consistent with the formation of more mono- and di-sulfidic linkages by the desulfuration process in comparison to the systems containing TMTD alone.

In the CBS–dithiobiuret systems, the total crosslink density and polysulfidic linkages are higher than for vulcanizates from CBS alone. This supports the higher modulus, tensile strength, hardness, and resilience, as well as the lower compression set and heat build-up values of the binary dithiobiuret vulcanizates. In this case also, DTB-III gives higher chemical crosslink density values consistent with its superior physical properties.

The lower free-sulfur concentration for the dithiobiuret systems cured at 150°C *vs.* the control mixes indicates improved vulcanization efficiency in these cases. Also, the lower zinc-sulfide sulfur concentration probably accounts for the lower concentration of monosulfidic linkages. In the chemical characterization studies of the systems containing carbon-black–dithiobiurets, it can be seen in Table X that the total crosslink density and polysulfidic linkages of vulcanizates containing dithiobiurets are higher, while monosulfide linkages are slightly lower than vulcanizates from TMTD alone. Both DTB-II and DTB-III systems give better crosslink density results than that of TMTD–thiourea.

CONCLUSIONS

It may be concluded that 1-phenyl-2,4-dithiobiuret and 1,5-diphenyl-2,4-dithiobiuret can be advantageously used as secondary accelerators in the sulfur vulcanization of SBR with

TABLE IX

PHYSICAL PROPERTIES OF THE MIXES CONTAINING FILLERS

Mix no.	300% modulus, MPa	Tensile, strength, MPa	Elongation at break, %	Hardness, Shore A	Compression set, %	Heat build-up, ΔT°C	Resilience, %	Tear strength, kN/m
I	9.70	16.40	483.85	65	20.46	29	48.75	73.35
II	7.30	14.2	494.09	63	21.76	25	49.37	58.50
III	9.93	17.68	490.20	65	21.16	29	50.63	59.70
IV	10.80	18.20	577.12	61	21.75	31	50.63	68.40

TABLE X

CHEMICAL CHARACTERIZATION OF VULCANIZATES CURED AT 150°C[a]

Mix no.	Total crosslink density, mmole/kg	Monosulfide linkages, mmole/kg	Disulfide linkages, mmole/kg	Poly-sulfide linkages, mmole/kg	Free sulfur, mmole/kg	Zinc-sulfide sulfur, mmole/kg
A_0	81.0	52.4	17.5	11.1	6.28	14.36
B_0	75.6	56.6	12.8	8.2	9.10	16.60
A_4	77.8	54.5	13.4	9.9	7.90	15.80
B_3	86.4	55.5	15.8	15.1	5.99	16.20
C_0	37.7	20.4	6.1	11.2	14.71	4.25
C_3	45.8	18.9	13.2	13.7	12.40	3.80
D_2	50.9	16.9	16.4	17.6	11.90	3.25
I	81.6	39.2	30.8	11.6	3.43	14.50
II	74.4	30.8	33.4	10.2	4.55	4.39
III	80.2	35.6	32.7	11.9	4.10	8.36
IV	83.3	37.5	31.7	14.1	2.50	12.13

[a] All concentrations reported as mmole/kg of rubber hydrocarbon.

TMTD or CBS as the primary accelerator. The introduction of dithiobiuret reduces considerably the optimum cure time, and practical cure systems with the optimum concentration of dithiobiuret have been developed. DTB-II is found to be more effective as a secondary accelerator than DTB-III with regard to the reduction in cure time. This suggest the importance of a nucleophilic reaction mechanism in these vulcanization systems. Tensile properties showed a general improvement in the binary systems containing dithiobiurets while other properties, *i.e.*, compression set, heat build-up, etc., gave favorable trends.

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