

A New Binary Accelerator System for the Sulfur Vulcanization of Natural Rubber Latex

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SYNOPSIS

Vulcanization of latex products are usually carried out at lower temperatures compared to dry rubber products. It has been suggested that, in latex vulcanization systems where thiourea is used as a secondary accelerator, it acts as a nucleophilic reagent facilitating the cleavage of the sulfur bonds in the primary accelerator like TMTD or CBS at lower temperature. But no conclusive proof is given to such a postulate. In the present study 1-phenyl-2,4-thiobiuret (DTB II) and 1,5-diphenyl-2,4-dithiobiuret (DTB III), which are more nucleophilic than thiourea and which vary in their nucleophilic reactivity, were studied as secondary accelerators along with tetramethyl thiuram disulphide (TMTD) and *N*-cyclohexylbenzothiazyl sulphenamide (CBS) in the vulcanization of natural rubber latex. These binary systems were found to be very effective in reducing the optimum vulcanization time. Also it was noted that 1-phenyl-2,4-dithiobiuret, which is more nucleophilic, is more reactive (as observed from the reduction in optimum cure time) as a secondary accelerator, indicating a nucleophilic reaction mechanism in the vulcanization reactions under review. The optimum dosages of the secondary accelerators required were derived. Physical properties like tensile strength, 300% modulus, and elongation at break of the latex vulcanizates were also studied. There is a definite advantage with respect to many of these properties for dithiobiuret systems compared to the systems containing TMTD alone or TMTD/thiourea. DTB III gives higher values in many of these physical properties than DTB II. Chemical characterization of the vulcanizates was also carried out to correlate the physical properties with the type of chemical crosslinks formed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The use of accelerators in rubber latex is basically different from their use in dry rubber.¹⁻⁵ The accelerators added to the latex mixture should become evenly distributed without causing the mixture to coagulate or to thicken. Ultra accelerators are frequently employed in latex mixtures to reduce the danger of scorching.⁶⁻⁹ Tetramethylthiuramdisulfide (TMTD) may be used to cure natural rubber latex compounds without the addition of sulfur or with the addition of a small amount of sulfur to prepare heat-resistant articles.¹⁰⁻¹² It may also be used to

prepare vulcanizates which are resistant to copper-catalyzed oxidative degradation. The vulcanization of latex using TMTD proceeds at relatively high temperature. It has been shown by Philpott¹³ that sulfur-containing nucleophiles like thiourea are able to activate vulcanization by TMTD, so that well-cured natural rubber vulcanizates may be produced rapidly at around 100°C.

He has also observed that sulfenamide accelerators, which do not vulcanize natural rubber latex in the absence of added sulfur or at very low dosages of sulfur, are also activated by thiourea to such an extent that the combination will effect cure at technologically useful rates. He found that a combination of cyclohexyl benzthiazyl sulfenamide (CBS) and thiourea, with or without the addition of elemental sulfur, can be used for the vulcanization of latex compounds at comparatively lower temperatures.

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from these matured compounds were vulcanized under standard conditions. In order to study the effect of temperature on the cure of these latex compounds, they were cured at 120 and 100°C. Cure characteristics of these films were then evaluated from the tensile strength/time relationship during cure. Tensile properties of vulcanizates like tensile strength, modulus, elongation at break, etc. were also evaluated and compared with the control. In order to understand the variation in physical properties of the different vulcanizates and to correlate them to the chemical crosslinks formed, chemical characterization of the vulcanizates has also been carried out.

EXPERIMENTAL

1-Phenyl-2,4-Dithiobiuret¹⁴ (DTB II)

Ammonium phenyl dithiocarbamate was first prepared by the interaction of carbondisulphide and aniline in ammoniacal medium at 0°C. The former 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 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 0.5 h when a clear solution resulted. This was then diluted with water (150 mL), filtered, and the filtrate acidified with concd hydrochloric acid (4 mL, 33%). The crude 1-phenyl-2,4 dithiobiuret obtained was dissolved in minimum quantity of 4% aq sodium hydroxide to remove any unreacted thiourea and filtered. The alkaline filtrate on acidification at 0°C afforded 1-phenyl-2,4-dithiobiuret which recrystallized from ethanol (mp 180°C).

1,5-Diphenyl-2,4-Dithiobiuret¹⁴ (DTB III)

Phenyl thiourea was prepared by the interaction of aniline with ammonium thiocyanate in hydrochloric acid. Phenyl isothiocyanate prepared as detailed in the above section (.025 mol) was added dropwise for 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 0.5 h when a clear solution resulted. This was diluted with water (150 mL) and filtered; the filtrate acidified with concd hydrochloric acid (4 mL, 33%), and the precipitated product collected and redissolved in minimum quantity of 4% aq sodium hydroxide to remove any unreacted phenyl thiourea.

This was filtered and the alkaline filtrate on acidification with hydrochloric acid at 0°C afforded 1,5-diphenyl-2,4-dithiobiuret, which recrystallized from ethanol (mp 143°C).

Centrifuged natural rubber latex of 60% dry rubber content and conforming to BS 5430-1981 was used in this study. Other compounding ingredients were of commercial grade. Two parts by weight of 10% potassium hydroxide solution were added to maintain the latex stock throughout the compounding and processing stages. Dispersions of zinc oxide, accelerators, and sulfur were added according to formulation given in Tables I and II. Thiourea and dithiobiurets were added as 10% aqueous solution. All the ingredients were added with slow and thorough stirring. After the addition of ingredients, the compounds were kept for maturation at room temperature for 48 h.

Latex films were prepared by casting the matured compound in shallow glass dishes: The film thickness was controlled in the range of 1–1.25 mm and were then vulcanized at 120 and at 100°C for specific time periods (up to 100 min) in an air oven. The tensile properties of the vulcanized latex film was determined using a Zwick Universal Testing Machine as per ASTM D 412-83. For these latex films, the optimum cure time was then found out from the

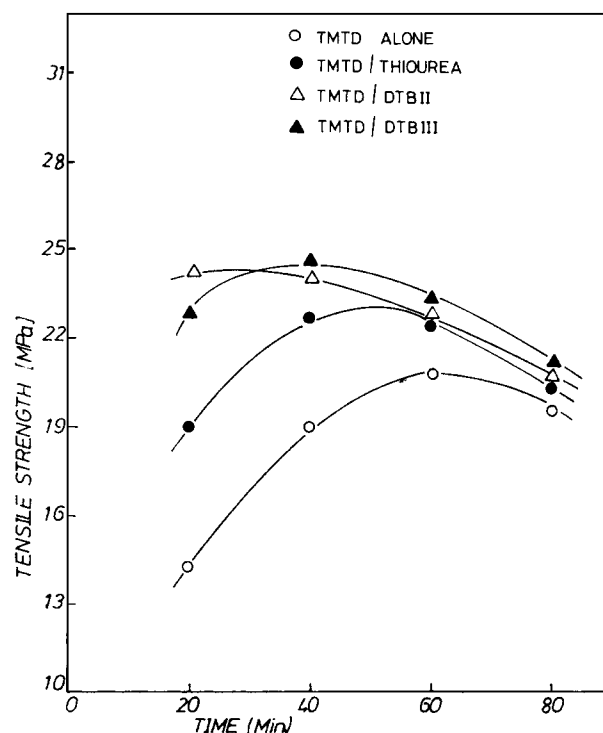


Figure 1 TMTD systems: variation of tensile strength of the vulcanizates with vulcanization time (120°C).

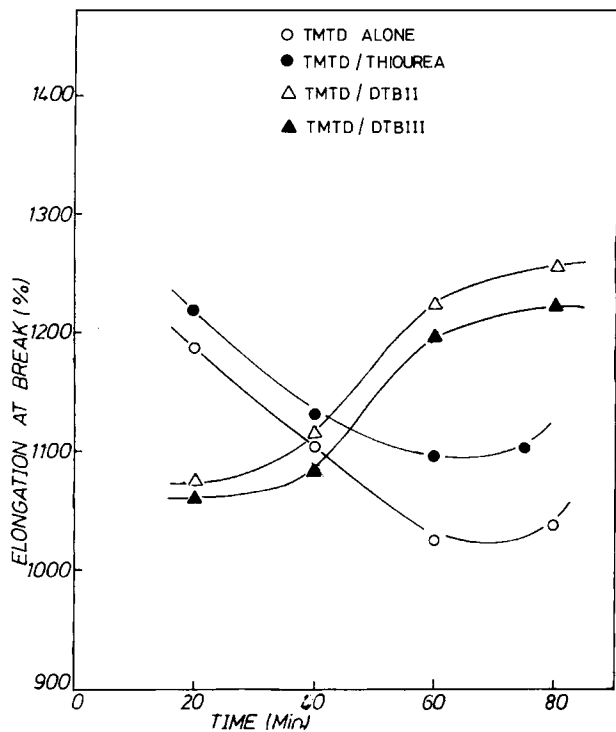


Figure 2 TMTD systems: variation of elongation at break with vulcanization time (120°C).

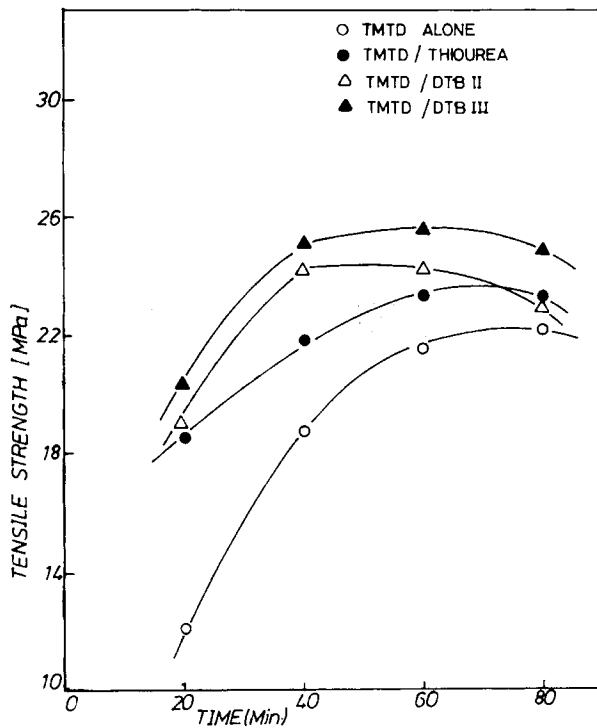


Figure 4 TMTD systems: variation of tensile strength of the vulcanizates with vulcanization time (100°C).

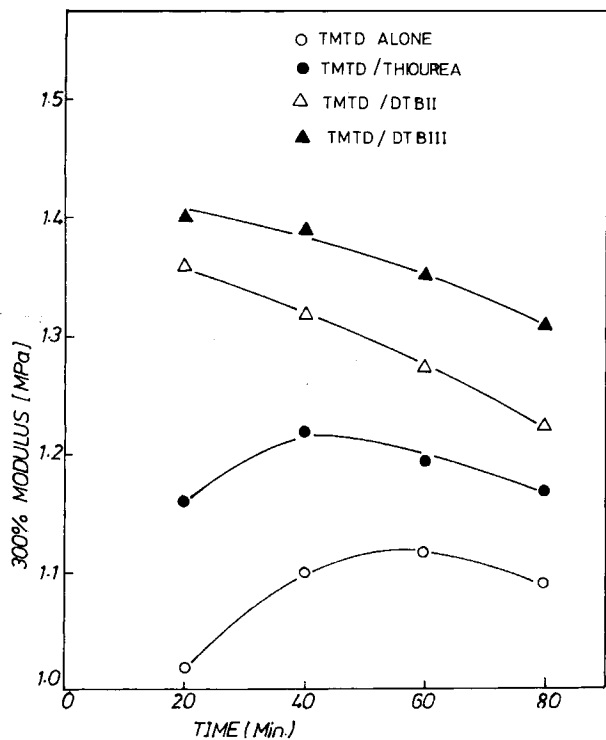


Figure 3 TMTD systems: variation of 300% modulus with vulcanization time (120°C).

tensile properties-time graph (Figs. 1-12). Tensile strength is plotted against time for vulcanization. From the graph, the time taken for attaining the optimum tensile strength is taken as the optimum cure time. To substantiate this cure time, the vulcanization time was also plotted against elongation at break and 300% modulus. The chemical crosslink density of these vulcanizates was also determined at optimum conditions using the equilibrium swelling method.¹⁶⁻¹⁸

RESULTS AND DISCUSSION

Cure Characteristics

The tensile properties time relationship at 120 and 100°C was tabulated for the systems containing TMTD alone as accelerator (Mix A0), TMTD/thiourea (Mix B0), TMTD/DTB II (Mix A3), TMTD/DTB III (Mix B3), CBS/thiourea (Mix D0), CBS/DTB II (Mix C3), and CBS/DTB III (Mix D3). These are given in Figures 1-12. It can be seen from Figure 1 that at 120°C the TMTD/DTB II system takes 20 min to attain optimum tensile strength while the TMTD/DTB III system

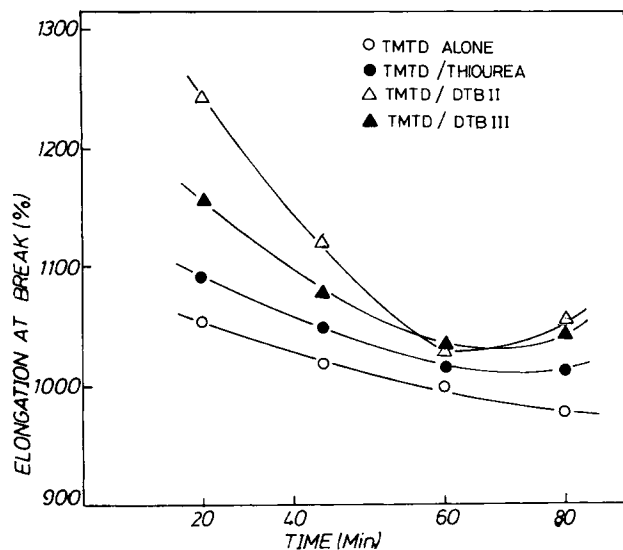


Figure 5 TMTD systems: variation of elongation at break with vulcanization time (100°C).

takes 30 min. The TMTD/thiourea system takes 45 min, and the system containing TMTD alone takes 60 min. At 100°C (Fig. 4) the times required for optimum tensile strength were found to be 40, 50, 60, and 70 min, respectively. From Figure 7 it can be seen that at 120°C the system containing

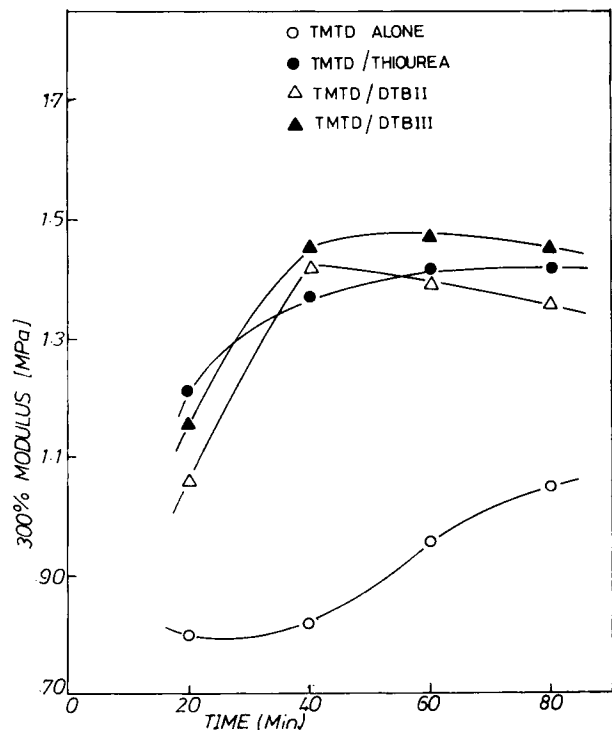


Figure 6 TMTD systems: variation of 300% modulus with vulcanization time (100°C).

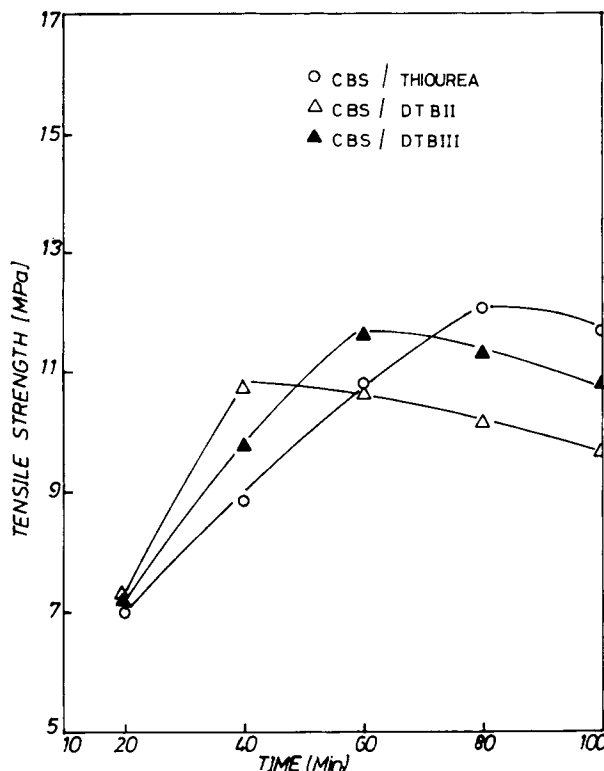


Figure 7 CBS systems: variation of tensile strength of the vulcanizates with vulcanization time (120°C).

CBS/DTB II takes 40 min, while the system containing CBS/DTB III takes 60 min to cure. The system containing CBS/thiourea takes 80 min. At 100°C (Fig. 10) these systems have taken 60, 80, and 90 min, respectively, to attain optimum tensile properties. The mix containing CBS alone as accelerator did not cure satisfactorily and hence was not included in the further study. These results indicate that these two dithiobiurets can be effectively used as secondary accelerators in the vulcanization of natural rubber latex containing TMTD or CBS as primary accelerator. There is substantial reduction in the optimum cure time when these secondary accelerators were incorporated. DTB II is more effective as an accelerator than DTB III pointing to a nucleophilic reactivity in the vulcanization reactions under review. This also confirms the view expressed by Philpot.¹³

Tensile Properties

The tensile properties of the latex vulcanizates with various concentrations of the dithiobiurets and cured at the optimum cure time are given in Tables III-VI. In the case of TMTD/dithiobiuret systems cured

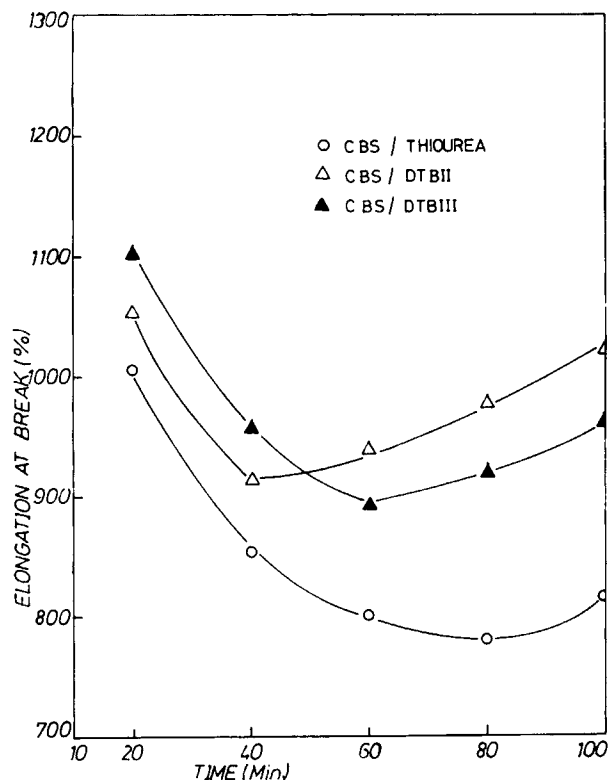


Figure 8 CBS systems: variation of elongation at break with vulcanization time (120°C).

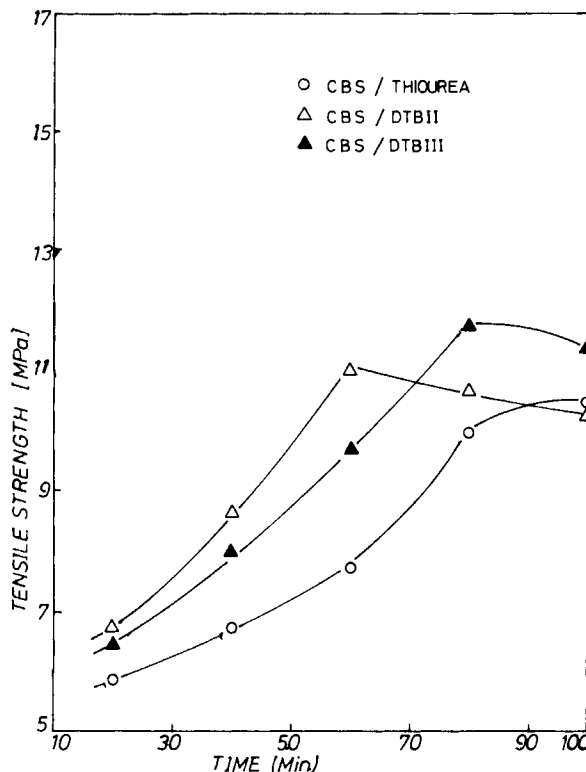


Figure 10 CBS systems: variation of tensile strength with vulcanization time (100°C).

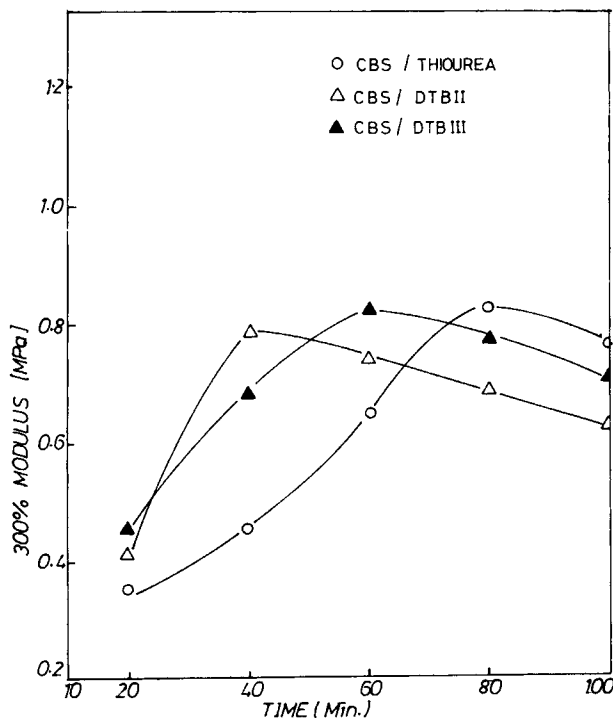


Figure 9 CBS systems: variation of 300% modulus with vulcanization time (120°C).

at 120°C, the tensile strength and 300% modulus increase as the dosage of dithiobiuret decreases and, after the optimum stage, decrease. As expected, elongation at break shows the reverse trend. When cured at 100°C, the same trend is also followed, but the tensile properties are better at this lower temperature. Five parts of DTB II (Mix A3) and 10 parts of DTB III (Mix B2) give more or less the optimum tensile properties and can be taken as the optimum dosages. Compared with TMTD alone and TMTD/thiourea systems, the systems containing optimum dosages of dithiobiurets give better tensile property values. In the case of the CBS/dithiobiuret system, the same trend is also followed, viz., first the tensile properties increase and, after the optimum level, decrease. In this case 10 parts of DTB II (Mix C2) and 15 parts DTB III (Mix D1) can be taken to be the optimum dosages. The systems containing optimum dosages of dithiobiurets give comparable values of tensile properties with that of CBS/thiourea system.

Chemical Characterization

Chemical characterization of the samples was carried out using the equilibrium swelling method as

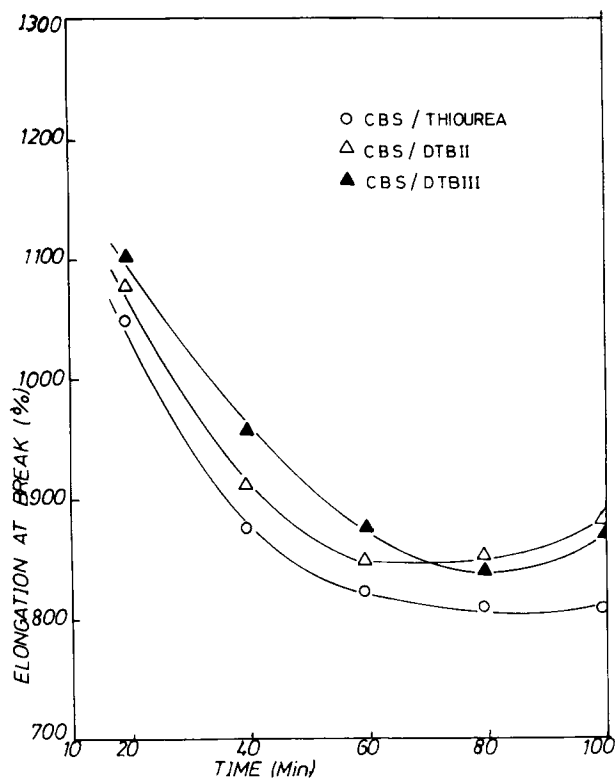


Figure 11 CBS systems: variation of elongation at break with vulcanization time (100°C).

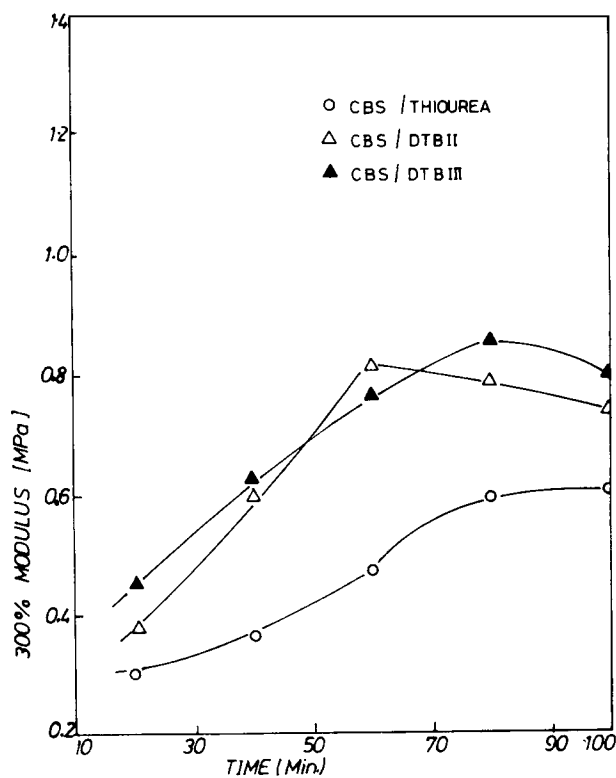


Figure 12 CBS systems: variation of 300% modulus with vulcanization time (100°C).

mentioned in the experimental section. Table VII shows the results obtained in the estimation of different chemical crosslinks, free sulfur, and zinc sulfide concentrations. It can be seen from the table that when cured at 120 and at 100°C, the total crosslink density and polysulfidic linkages of the vulcanizates containing dithiobiurets are more than those containing TMTD alone or TMTD/thiourea. The increase in the tensile properties in the systems

containing dithiobiurets can thus be attributed to the higher concentration of polysulfidic linkages.

In the case of the systems containing CBS and dithiobiurets, concentration of total crosslinks and polysulfidic linkages (cured at 120°C) are lower compared to the thiourea system. But at 100°C these values are better. The lower tensile strength values offered by the dithiobiurets in these systems at 120°C may be attributed to the lower polysulfidic

Table III Tensile Properties of Vulcanizates Containing TMTD/DTB-II

Mix No.	300% Modulus (MPa)		Tensile Strength (MPa)		Elongation at Break (%)	
	120°C	100°C	120°C	100°C	120°C	100°C
A0	1.12	1.05	20.7	22.1	1025	980
B0	1.22	1.42	23.0	23.3	1120	1015
A1	1.26	1.37	23.1	23.30	1230	1190
A2	1.28	1.40	23.4	23.70	1172	1160
A3	1.36	1.42	24.3	24.30	1074	1122
A4	1.25	1.30	20.6	24.15	1392	1221

Table IV Tensile Properties of Vulcanizates Containing TMTD/DTB-III

Mix No.	300% Modulus (MPa)		Tensile Strength (MPa)		Elongation at Break (%)	
	120°C	100°C	120°C	100°C	120°C	100°C
A0	1.12	1.05	20.7	22.1	1025	980
B0	1.22	1.42	23.0	23.3	1120	1015
B1	1.55	1.60	24.8	25.8	1039	1010
B2	1.48	1.90	25.3	26.2	1020	995
B3	1.39	1.47	24.5	25.4	1085	1036
B4	1.38	1.38	22.3	24.8	1187	1120

Table V Tensile Properties of Vulcanizates Containing CBS/DTB-II

Mix No.	300% Modulus (MPa)		Tensile Strength (MPa)		Elongation at Break (%)	
	120°C	100°C	120°C	100°C	120°C	100°C
D0	0.83	0.60	12.10	10.50	780	810
C1	0.90	0.92	10.90	11.60	860	825
C2	0.96	0.99	11.20	11.80	870	842
C3	0.79	0.81	10.75	11.50	915	845
C4	0.52	0.64	9.30	9.90	940	915

Table VI Tensile Properties of Vulcanizates Containing CBS/DTB-III

Mix No.	300% Modulus (MPa)		Tensile Strength (MPa)		Elongation at Break (%)	
	120°C	100°C	120°C	100°C	120°C	100°C
D0	0.83	0.60	12.1	10.50	780	810
D1	1.10	1.12	12.05	12.10	810	802
D2	0.95	1.03	11.80	11.90	850	825
D3	0.82	0.85	11.60	11.75	890	837
D4	0.60	0.68	10.80	11.20	915	870

concentration. The enhancement of tensile strength at 100°C is evident in the increase in polysulfidic crosslinks.

Table VII Chemical Characterization of the Vulcanizates

Cure Temp	Mix No.	Total Crosslink Density (mmol/kg RH)	Poly Sulfide Linkages (mmol/kg RH)	Free Sulfur Concentration (mmol/kg RH)	Zinc Sulfide Concentration (mmol/kg RH)
120°C	A0	51.5	20.6	20.5	8.10
	B0	57.8	21.6	24.2	6.50
	A3	60.2	23.7	19.3	11.50
	B2	66.4	26.4	17.5	12.40
100°C	A0	51.8	20.9	20.8	8.20
	B0	60.2	22.5	23.3	6.20
	A3	61.6	25.4	18.4	11.80
	B2	70.5	29.8	15.2	13.20
120°C	D0	29.5	12.8	10.2	7.40
	C2	27.4	10.5	12.5	5.50
	D1	29.90	12.1	11.4	6.20
100°C	D0	22.4	10.8	12.8	4.80
	C2	28.0	11.2	9.4	6.80
	D1	30.4	13.4	8.2	8.50

In TMTD/dithiobiuret systems, free sulfur concentration is lower than that of the system containing TMTD alone or TMTD/thiourea, which indicate a more effective utilization of sulfur in the former. The higher concentration of zinc sulfide sulfur in the systems containing dithiobiurets indicates higher rate of desulfuration resulting in higher concentration of mono and disulfidic linkages. In CBS/dithiobiuret systems also lower free sulfur values and higher zinc sulfide sulfur concentration is obtained at the lower vulcanization temperature of 100°C.

CONCLUSION

From the above results it can be seen that 1-phenyl-2,4-dithiobiuret and 1,5-diphenyl-2,4-dithiobiuret are very effective as secondary accelerators in the sulfur vulcanization of natural rubber latex, where TMTD or CBS are used as primary accelerators. Incorporation of small amounts of dithiobiurets reduces the optimum cure time considerably, and practical cure systems have been developed which will be of definite advantage to the NR latex product manufacturing industry. DTB II is found to be a more active accelerator than DTB III, indicating a nucleophilic reaction mechanism in these vulcanization reactions. Evaluation of the tensile properties of the vulcanizates containing optimum concentra-

tion of the dithiobiurets also gave satisfactory results.

REFERENCES

1. H. H. Abernathy, *Rubber Chem. Technol.*, **15**, 195 (1941).
2. H. H. Abernathy, *Rubber Age N.Y.*, **50**, 195 (1941); **52**, 405 (1943).
3. H. Brown, Udyllite Corp., Br. Pat. 564232.
4. Cadwell, Br. Pats. 279815 and 298837 (1928).
5. C. Coleman, Br. Pat. 410454.
6. W. Schaefer, *Gummi Z.*, **55**, 400 (1941).
7. Schidrowitz, *India Rubber J.*, **62**(8), 25 (1920).
8. R. J. Sibley, *Trans. Inst. Rubber Ind.*, **13**, 453 (1940); *Rubber Age N.Y.*, **47**, 22 (1940).
9. Smith, U.S. Pat. 1562262 (1925); Br. Pat. 239849 (1924).
10. R. O. Babbit, *Rubber Age N.Y.*, **48**, 90 (1940).
11. J. R. Dunn, *Trans. IRI*, **34**, 249 (1958).
12. B. L. Babitskii and L. E. Uinitskii, *Sov. Rubber Technol.*, **20**(3), 28 (1961).
13. M. W. Philpott, in *Proc. Rubber Technol. Conf.*, London, 1962, p. 470.
14. C. P. Joshua, E. Prasannan, and S. K. Thomas, *Indian J. Chem.*, **21B**, 649 (1982).
15. A. P. Kuriakose and George Mathew, *Indian J. Technol.*, **26**, 344 (1988).
16. B. Ellis and G. W. Welding, in *Techniques of Polymer Science*, Soc. Chem. Ind., London, 1960, p. 46; *Rubber Chem. Technol.*, **37**, 571 (1964).
17. D. S. Campbell, *J. Appl. Polym. Sci.*, **13**, 120 (1969).
18. H. E. Adam and B. L. Johnson, *Rubber Chem. Technol.*, **26**, 741 (1953).

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