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Effect of 1-Substituted and 1,5-Disubstituted 2,4-Dithiobiurets-N-Cyclohexyl Benzthiazyl Sulphenamide (CBS) Binary Accelerator Systems in the Vulcanization of NR/SBR Blends

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1-phenyl-2,4-dithiobiuret · 1,5-diphenyl-2,4-dithiobiuret · N-cyclohexyl benzthiazyl sulphenamide · Secondary accelerator · NR/SBR blend

1-Phenyl-2,4-dithiobiuret · 1,5-Diphenyl-2,4-dithiobiuret · Benzothiazyl-N-cyclohexylsulfenamid · Zweitbeschleuniger · NR/SBR-Verschnitt

1-phenyl-2,4-dithiobiuret (DTB-II) and 1,5-diphenyl-2,4-dithiobiuret (DTB-III) were studied as secondary accelerators along with N-cyclohexyl benzthiazyl sulphenamide (CBS) in the vulcanization of a blend of NR and styrene-butadiene rubber. These binary systems were found to reduce the optimum vulcanization time considerably. The more nucleophilic reagent viz. 1-phenyl-2,4-dithiobiuret reduced the vulcanization time more. In both cases the optimum dosage of the secondary accelerator was derived. Physical properties like tensile strength, modulus, elongation at break, hardness, compression set, heat build up, resilience etc. of the vulcanizates were studied before and after ageing. There is substantial increase in many of these properties when these binary systems are used. Chemical characterization of the vulcanizates was also carried out to correlate the physical properties with the ty[illegible] chemical crosslinks formed.

Die Wirkung von Beschleunigergemischen aus 1-substituierten bzw. 1,5-disubstituierten 2,4-Dithiobiureten und Benzothiazyl-N-cyclohexylsulfenamid (CBS) auf die Vulkanisation von NR/SBR-Verschnitten

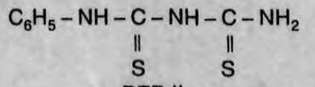
1-Phenyl-2,4-dithiobiuret (DTB-II) und 1,5-Diphenyl-2,4-dithiobiuret (DTB-III) wurden als Zweitbeschleuniger für Benzothiazyl-N-cyclohexylsulfenamid (CBS) zur Vulkanisation eines Verschnitts aus NR und Styrol-Butadienkautschuk eingesetzt. Die Kombination verringert die optimale Vulkanisationszeit erheblich, das stärker nucleophile 1-Phenyl-2,4-dithiobiuret wirkt am besten. Die optimale Dosierung des jeweiligen Zweitbeschleunigers wurde ermittelt. Die physikalischen Eigenschaften wie Reißfestigkeit, Spannungswert, Reißdehnung, Härte, Druckverformungsrest, Heat-build up, Rückprallelastizität usw. wurden vor und nach einer Wärmealterung bestimmt. Viele Eigenschaften werden bei Verwendung der Beschleunigerkombination verbessert. Es wurde versucht, die physikalischen Eigenschaften zur Netzwerkstruktur in Beziehung zu setzen.

1 Introduction

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. It has been proven that accelerators in which sulphur is combined as S-C, C-S-C or S-N are virtually inactive at temperatures below 100 °C because of the high thermal stability of their S-bonds. It was also shown that sulphur containing nucleophiles enable such accelerators to operate at lower vulcanization temperature.

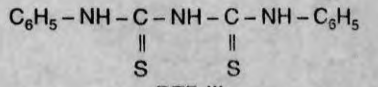
In his studies on different nucleophiles *Philpot* [1] has shown that thiourea is very reactive in the vulcanization of NR latex with TMTD. Similar reactivity was also observed in accelerators containing S-C linkage and sulphenamide type accelerators containing the S-N linkage. Heat resistant sulphurless vulcanizates with superior ageing properties were also obtained with the help of thiourea derivatives. Though a number of thiourea derivatives have been tried in rubber vulcanization, the activating effect of dithiobiuret derivatives of thiourea which are more nucleophilic than thiourea is not reported in the literature.

A few dithiobiurets were synthesised in our laboratory according to *Joshua* et al. [2] and their acceleration activity was evaluated in NR [3] and styrene butadiene rubber (SBR) [4]. DTB-II and DTB III gave promising results when they were tried as secondary accelerators in NR and SBR. In view of the practical significance in rubber vulcanization, we extended this study to NR/SBR blends.



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

DTB-II



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

DTB-III

It is generally recognized that a single elastomer cannot meet all the requirements like oil and chemical resistance, dynamic properties, weathering resistance etc. of a rubber product. Blends of rubbers are widely used to obtain a balance of properties including cost, and to overcome processing difficulties. NR and SBR being general purpose rubbers can be usefully blended if the fundamental differences and similarities between them are recognized. In the vulcanization of NR/SBR blends, NR phase takes a large share of curatives leaving the SBR phase slightly under crosslinked [5]. This necessitates a more active accelerator or a special binary accelerator system to obtain uniform cure. We utilized the systems containing dithiobiurets and CBS in the vulcanization of a 50:50 blend of NR and SBR-1502. In this paper we report the results of this study.

2 Experimental

Tables 1 and 2 give the composition of the various mixes. In an attempt to find out the optimum concentrations of the dithiobiurets required in these compounds, the following mixes were prepared. Mix C_0 contains 1,5 phr of CBS alone as accelerator. Mixes $C_1 - C_4$ contain different concentrations of DTB-II ranging from 1,5 – 0,25 phr with 1,5 phr CBS. Mixes $D_1 - D_4$ contain different concentrations of DTB-III ranging from 1,5 – 0,25 phr with 1,5 phr CBS. Trial mixes were also prepared without CBS, but they cured very slowly and hence were abandoned. We evaluated the cure characteristics, vulcanizate properties, and the chemical characterization of the various combinations.

Table 1. **Formulation of the mixes**

Ingredients	C_0	C_1	C_2	C_3	C_4
NR	50	50	50	50	50
SBR 1502	50	50	50	50	50
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
CBS	1,5	1,5	1,5	1,5	1,5
DTB-II	–	1,5	1,0	0,5	0,25
Sulphur	0,5	0,5	0,5	0,5	0,5

Table 2. **Formulation of the mixes**

Ingredients	C_0	D_1	D_2	D_3	D_4
NR	50	50	50	50	50
SBR 1502	50	50	50	50	50
Zinc Oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
CBS	1,5	1,5	1,5	1,5	1,5
DTB-III	–	1,5	1,0	0,5	0,25
Sulphur	0,5	0,5	0,5	0,5	0,5

The optimum cure time for the various mixes at 150 and 120 °C was determined using a Monsanto rheometer (R 100). The cure curves are given in *Figures 1 – 4*. Scorch time of the mixes at 120 °C was evaluated using a Mooney viscometer. The cure characteristics are given in *Ta-*

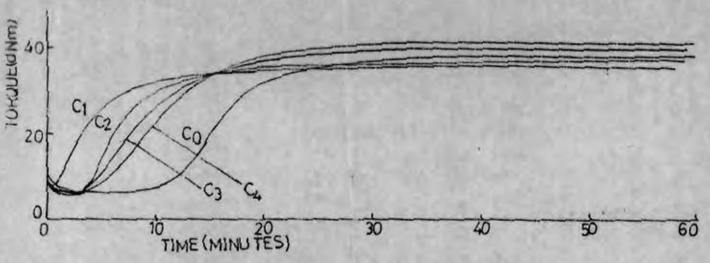


Figure 1. Rheographs of the mixes containing CBS-DTB II at 150 °C

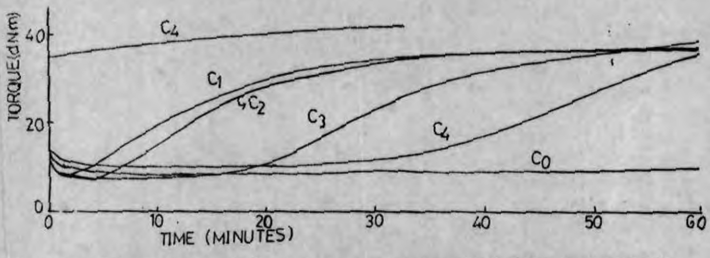


Figure 2. Rheographs of the mixes containing CBS-DTB II at 120 °C

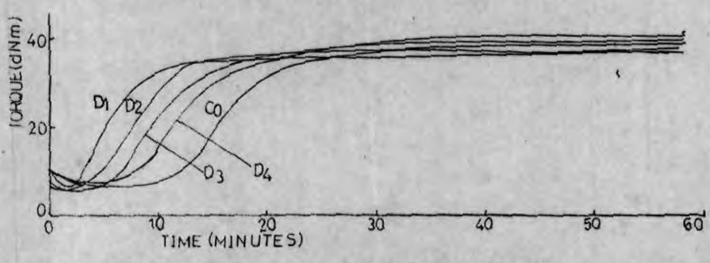


Figure 3. Rheographs of the mixes containing CBS-DTB III at 150 °C

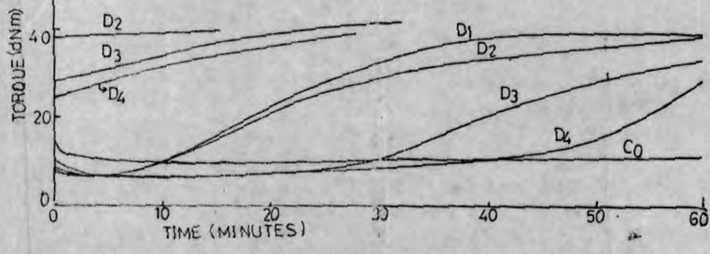


Figure 4. Rheographs of the mixes containing CBS-DTB III at 120 °C

bles 3 and 4. The NR used in the experiment is solid block rubber conforming to ISNR-5. SBR used is Synaprene-1502. NR was first masticated to a Mooney viscosity of 40 and then blended with SBR. The mixes were prepared on a laboratory size two roll mixing mill (30 cm × 15 cm) at a friction of 1:1,25 according to the procedure given in ASTM D15-62T. Vulcanization was carried out using a steam heated press having 18" × 18" platens maintained at 150/120 °C and at a pressure of 4,5 MPa. Tensile properties of the various vulcanizates were determined according to ASTM D412-51T using dumbbell specimens in a Zwick universal testing machine at a pulling rate of 500 mm/min at room temperature [30 °C]. Samples were punched from vulcanized sheets parallel to the grain direction using a dumbbell die (C type). Tear resistance was determined by ASTM method D624-48 using unnicked 90° angle test pieces. Tear resistance is reported in N/mm.

Shore A type durometer was used for determination of hardness. Readings were taken after 15 s of the indentation when firm contact had been established with the specimen. The method employed is ASTM D676-52T. Dunlop tripsometer (BS 903 pt. 22, 1950) was used to measure rebound resilience, keeping the temperature at 35 °C. For determination of compression set the samples 1,25 cm thick and 2,8 cm diameter in duplicate, compressed to constant deflection (25 %), were kept for 22 h in an air oven at 70 °C (ASTM D395-61-method B). After the heating period, the samples were taken out, cooled to room temperature for 0,5 h and the final thickness was measured. Heat-build up was measured using a Goodrich flexometer following ASTM D623-67, keeping the oven temperature at 50 °C, stroke-adjusted to 4,45 mm and the load to 100 N. Ageing of the samples was carried out at 70 °C for 96 h in a tubular ageing oven according to ASTM D-865.

The chemical crosslink density was determined at optimum conditions using the equilibrium swelling data as follows: Samples of approximately 1 cm diameter, 0,20 cm thickness and 0,20 g weigh[illegible]re punched out from the central portion of the vulcanizate and allo[illegible] to swell in solvent (benzene) containing 0,1 % phenyl-β-napthyl-amine (PBN). After 24 h, the solvent containing PBN was replaced by pure solvent and after another 2 h swelling was stopped. The swollen samples were weighed, solvent removed in vacuum and the sample weighed again. The volume fraction of rubber (Vr) in the swollen network was then calculated by the method reported by *Ellis* and *Welding* [6] from the following equation:

$$Vr = \frac{(D\text{-}FT)\,\varrho r^{-1}}{(D\text{-}FT)\,\varrho r^{-1} + Ao\,\varrho s^{-1}}$$

where T = weight of the test specimen
D = weight of the swollen test specimen
F = weight fraction of insoluble components
Ao = weight of the absorbed solvent corrected for the swelling increment

ϱr = Density of test specimen
ϱs = Density of solvent

The values of ϱr and ϱs taken are

ϱ (NR) = 0,92 g/cm³
ϱr (SBR) = 0,94 g/cm³
ϱs (benzene) = 0,875 g/cm³

The crosslink density $\frac{1}{2MC}$ was then determined from Vr using the Flory Rehner equation [7].

$$\ln(1\text{-}Vr) + Vr + \chi r^2 = \frac{\varrho Vs(Vr)^{1/3}}{Mc}$$

Table 3. **Cure characteristics of the mixes containing CBS dithiobiurets at 150 °C**

Mix. No.	C_0	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4
Min. torque (dNm)	7,0	7,5	8,0	6,0	7,0	6	7	5	7
Max. torque (dNm)	39,0	36	38,0	37,0	39,0	37	40	37	39
Induction time, t_1 (min)	11,5	1,5	2,0	3,5	6,0	2,5	2,5	5,5	7,5
Rheometric scorch time, t_2 (min)	12,5	2,0	2,5	4,0	6,5	3,0	3,0	6,0	8,5
Optimum cure time, t_{90} (min)	25,5	11,0	12,0	14,0	17,0	13,5	14,0	17,5	20,5
Cure rate index	7,69	11,11	10,33	10,0	9,52	9,52	9,09	8,70	8,33
Reversion at 170 °C (No. of units reverted in 5 min)	1	–	–	0,5	1,0	–	–	0,5	1

Table 4. **Cure characteristics of the mixes containing CBS dithiobiurets cured at 120 °C**

Mix. No.	C_0	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4
Min. torque (dNm)	–	9	8	8	10	6	8	6	9
Max. torque (dNm)	–	38	39	41	43	42	44	42	44
Induction time, t_1 (min)	–	3,5	5,5	16,0	29,5	6	10	25	43
Optimum cure time, t_{90} (min)	–	35,0	39,5	56,0	75,0	44,5	56,0	83,0	106,0
Cure rate index	–	3,28	2,99	2,67	2,44	2,74	2,25	2,15	1,92
Mooney scorch time, t_5 (min)	–	4,5	6,0	18,5	34,0	8,0	11,5	36,5	54.0

where Vs = Molar volume of solvent, Vs (benzene) = 90 mL/mol, and χ = the parameter characteristic of interaction between rubber and solvent [8]. For a 50/50 NR/SBR blend in benzene, this parameter was taken as 0,38.

The concentration of polysulphide crosslinks was estimated from the change in the crosslink density of the vulcanizate before and after treatment with propane-2-thiol and piperidine which cleaves the polysulphidic crosslinks in the network [9, 10]. Vulcanizate sample weighing about 0,2 – 0,3 g was allowed to stand in excess of solvent (benzene) containing 0,1 % PBN for 24 h at room temperature. The solvent was replaced by a solution (100 mL) of 0,4 mol propane-2-thiol and piperidine in benzene containing 0,5 % PBN for 2 h. On completion of reaction, the sample was removed from the reagent solution, washed with petroleum ether (40 – 60 °C) four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. The specimen was then kept in excess of the solvent for 24 h, and finally extracted for 2 h in pure solvent. The swollen sample was weighed, solvent removed in vacuum and the sample weighed again. The volume fraction of rubber (Vr) was then determined as before and the crosslink density was determined.

The determination of crosslink density before and after treatment with 1-hexane thiol gives the concentration of monosulphide linkage [9, 10]. Sinc[illegible]e concentration of polysulphidic linkages was determined befo[illegible]he concentration of disulphidic linkages could also be estimated. For determining monosulphidic linkages vulcanizate sample weighing about 0,2 – 0,3 g was allowed to stand in 100 mL of 1-hexanethiol in piperidine (1 mol solution) containing 0,5 % PBN for 48 h at room temperature. The mixture was agitated occasionally. On completion of reaction the sample was removed from the reagent solution, washed with petroleum ether (40 – 60 °C) four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. Then the specimen was kept in excess solvent (benzene) containing 0,1 % PBN for 24 h. Finally the specimen was kept in pure solvent for 2 h and swollen sample weighed. Then the solvent was removed in vacuum and the deswollen sample weighed again. The volume fraction of rubber in the swollen network (Vr) was then determined as before and the crosslink density was calculated.

Free sulphur in the vulcanizate was determined iodometrically by converting it to sodium thiosulphate according to ASTM D297-72 A. Zinc sulphide sulphur was determined iodometrically through the formation of cadmium sulphide as described in BS 902 pt 1310-1958.

3 Results and discussion

3.1 [illegible]e characteristics

The cure characteristics of various mixes at 150 and 120 °C were evaluated using a Monsanto rheometer (R-100) and the cure curves obtained are given in the Figures 1 – 4. The cure characteristics evaluated are given in the Tables 3 and 4. The results clearly indicate the acceleration effect of the dithiobiurets in the vulcanization of NR/SBR blends. Of the two dithiobiurets studied, DTB-II is found to be a more active accelerator indicating a nucleophilic reaction mechanism in this vulcanization reaction. The optimum cure time for CBS alone is 25,5. The addition of 1,5 phr DTB-II reduces it to 11 min, while DTB-III reduces it to 13,5 min. 0,5 phr DTB-II and 1 phr DTB-III can be taken to be the optimum concentrations. The systems containing dithiobiurets show better reversion resistance. At 120 °C, with increase in concentration of dithiobiurets cure time is appreciably reduced but the compound containing CBS alone cured so slowly that a comparison was not possible.

3.2 Tensile and other physical properties

The tensile properties of vulcanizates cured at 150 and 120 °C are given in the *Figures 5 – 7*. A decrease in tensile strength and 300 % modulus is observed with increase in the concentration of dithiobiurets. As expected the elongation at break is showing the reverse trend. But at the optimum dosage of 0,5 phr of DTB-II and 1 phr of DTB-III, comparable values of these properties are obtained with regard to the reference mix. The percentage retention in tensile properties is higher for both dithiobiurets. At 120 °C the same trend is followed, too, but here the tensile properties are higher than those at 150 °C. This may be attributed to the formation of more polysulphidic linkages at lower temperature as seen from Table 7.

Other physical properties are given in the *Tables 5 and 6*. In the vulcanizates containing dithiobiurets the physical properties

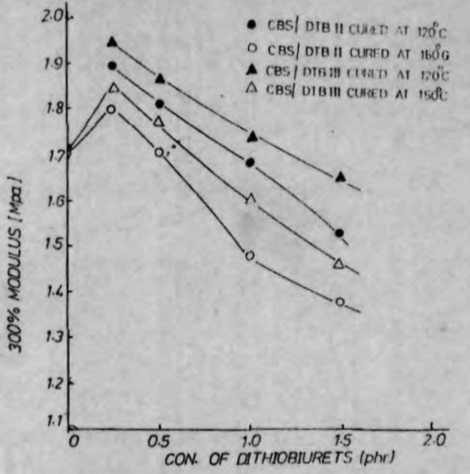


Figure 5. Variation of 300 % modulus of the vulcanizates with concentration of dithiobiurets

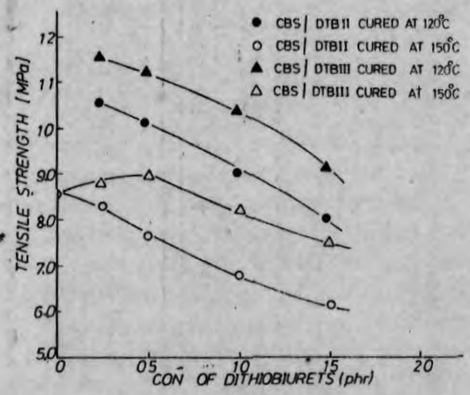


Figure 6. Variation of tensile strength of the vulcanizates with concentration of dithiobiurets

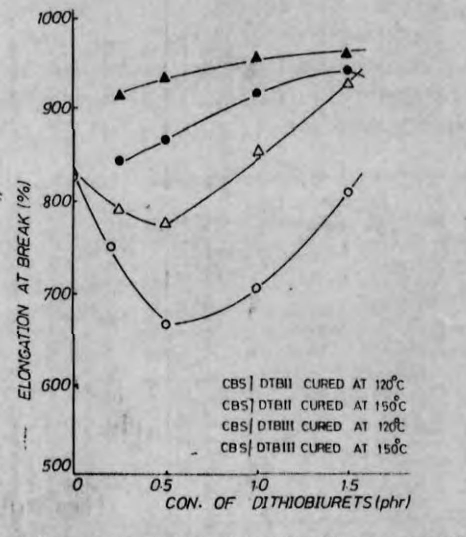


Figure 7. Variation of elongation at break with concentration of dithiobiurets

Table 5. **Physical properties of vulcanizates containing CBS/dithiobiurets cured at 150 °C**

Mix. No.	C_0	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4
Hardness (Shore A)	31	28	29	30	31	30	33	32	32
Compression set (%)	22,70	28,17	24,65	23,20	22,10	23,54	19,34	20,20	21,98
Heat build up (ΔT °C)	28	34	31	28	25	29	27	33	36
Resilience (%)	58,14	55,07	59,42	63,13	65,53	65,45	67,38	61,40	53,77
Tear strength (N/mm)	22,79	21,06	21,76	22,05	22,35	25,15	24,81	24,32	23,92

Table 6. **Physical properties of vulcanizates containing CBS/dithiobiurets cured at 120 °C**

Mix. No.	C_0	C_1	C_2	C_3	C_4	D_1	D_2	D_3	D_4
Hardness (Shore A)	–	30	31	33	33	34	36	36	34
Compression set (%)	–	22,80	21,50	18,26	19,09	18,50	17,40	17,80	18,40
Heat build up (ΔT °C)	–	30	28	24	22	26	24	28	32
Resilience (%)	–	53,16	56,15	62,70	64,40	64,25	66,40	62,10	53,40
Tear strength (N/mm)	–	21,53	21,95	22,45	23,85	26,30	26,51	26,22	25,82

such as hardness, resilience, tear strength compression set and heat build up are generally increasing with decrease in the concentration of dithiobiurets. Samples containing DTB-III give better results than those of DTB-II. At 120 °C these properties of the mixes containing dithiobiurets are better compared to those at 150 °C.

3.3 Chemical characterization

The total chemical crosslink density and different types of crosslinks like mono-, di-, and polysulphide linkages free, sulphur and zinc sulphide sulphur were evaluated for the vulcanizates containing CBS alone and for the systems containing optimum concentration of dithiobiurets. The results are given in *Table 7*. At 150 °C, the vulcanizates containing DTB-II have lower crosslink density and monosulphide linkages than those of CBS alone, while those containing DTB-III have higher values. There are more di- and polysulphide linkages for both dithiobiuret systems. This is in agreement with the slightly lesser values of tensile strength of DTB-II systems and higher values for the DTB-III systems. In the DTB-II systems free sulphur concentration is higher and zinc sulphide sulphur concentration is lower than that of the control indicating the less efficient utilization of sulphur. The opposite trend is seen in DTB-III showing more effective utilization of sulphur in these systems.

Table 7. **Chemical characterization of the vulcanizates**

Cure temp. (°C)	Mix No.	Total crosslink density (M. mole/ kg. RH)	Mono sulphide linkages (M. mole/ kg. RH)	Disulphide linkages (M. mole/ kg. RH)	Poly sulphide linkages (M. mole/ kg. RH)	Free sulphur con. (M. mole/ kg. RH)	Zinc sulphide sulphur conc. (M. mole/ kg. RH)
150	C_0	40,5	22,20	5,90	12,40	9,46	4,30
	C_3	38,2	15,90	8,70	13,60	10,68	3,60
	D_2	43,2	22,80	6,20	14,20	8,30	4,0
120	C_3	39,7	18,40	6,40	14,40	4,20	3,88
	D_2	45,6	23,70	6,20	15,70	8,90	4,25

4 Conclusions

1. 1-phenyl-2,4-dithiobiuret and 1,5-diphenyl-2,4-dithiobiuret can be used as very effective secondary accelerators along with CBS in a 50:50 blend of NR and SBR. An appreciable reduction in the optimum cure time is found.
2. 1-phenyl-2,4-dithiobiuret which is more nucleophilic is more effective accelerator indicating a nucleophilic reaction mechanism in the systems under review.
3. Many physical properties of the vulcanizates are improved at the optimum dosage of these dithiobiurets.
4. Ageing resistance and reversion resistance of the vulcanizates are improved by the addition of these dithiobiurets.

References

[1] M. W. Philpot: IRI, IVth Rubber Technology Conference, London, 39th article.
[2] C. P. Joshua, E. Presannan and S. K. Thomas, Indian J. Chem. **21 B** (1982) 649.
[3] A. P. Kuriakose and George Mathew, Indian J. Techn. **26** (1988) 344.
[4] George Mathew: paper presented in the First Kerala Science Congress, Cochin (1988).
[5] J. B. Gardiner, Rubber Chem. Technol. **43** (1970) 370.
[6] B. Ellis and G. W. Welding: Techniques of Polymer Science. Soc. Chem. Ind., London (1964) p. 46.
[7] P. J. Flory and J. Rehner, J. Chem. Phys. **11** (1943) 512.
[8] C. J. Sheelan and A. L. Basio, Rubber Chem. Technol. **39** (1966) 144.
[9] N. M. Mathew, M. K. Bhowmick and S. K. De, Rubber Chem. Technol. **54** (1982) 51.
[10] V. Brajko, V. Duchacek, J. Taue and E. Tumova, Int. Polym. Sci. Technol. **7** (1980) 64.

EPF '92 in Baden-Baden
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Polymere mit supramolekularer Architektur, neue Entwicklungen in der Charakterisierung von Polymeren sowie computergestützte Polymerforschung stehen als thematische Schwerpunkte auf dem Programm des internationalen Symposiums „EPF '92" vom 27. September bis 2. Oktober 1992 in Baden-Baden. Zu diesem 4. European Polymer Federation-Symposium über polymere Materialien werden rund 500 Wissenschaftler – Chemiker, Physiker und Ingenieure – aus Hochschulinstituten, außeruniversitären Forschungseinrichtungen und der Industrie erwartet. Vorsitzender des wissenschaftlichen Komitees und der Tagung ist Professor Dr. H. W. Spiess vom Max-Planck-Institut für Polymerforschung (MPI) in Mainz. Die Federführung in der Organisation hat die Gesellschaft Deutscher Chemiker (GDCh), Fachgruppe „Makromolekulare Chemie", übernommen.

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