

# Effect of 1-phenyl-2,4-dithiobiuret as secondary accelerator on cure characteristics and vulcanisate properties of natural rubber–styrene/ butadiene rubber blends

Abi Santhosh Aprem, Kuruvilla Joseph, Sabu Thomas, Nektaria Marianthi Barkoula and J. Karger-Kocsis

Blends of natural rubber and styrene/butadiene rubber have been cured using a new binary accelerator system containing 1-phenyl-2,4-dithiobiuret (DTB). This new accelerator was synthesised and used in combination with sulphenamides such as dicyclohexyl benzothiazyl sulphenamide, tertiary butyl benzothiazole sulphenamide and morpholinothio benzothiazole sulphenamide. A significant reduction in cure time was observed with the addition of DTB. Network characterisation of the vulcanisates was carried out by the estimation of cross-link density and relative proportions of crosslinks. The mechanical properties of the vulcanisates improved upon addition of DTB. Dynamic mechanical analysis was carried out to study the effect of the new accelerator on entanglement density and modulus. Based on the processing behaviour, mechanical properties and chemical characterisation it was found that DTB could be effectively used as a secondary accelerator in the curing of NR–SBR blends.

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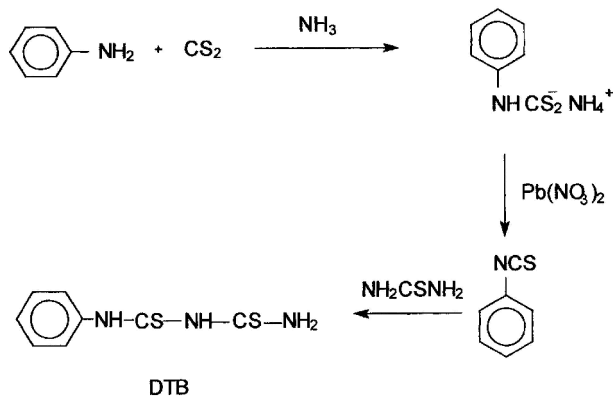
## INTRODUCTION

Scientific and commercial progress in the field of polymer blends over the past few decades has been tremendous. New materials can be developed and implemented more rapidly and economically by the process of blending. The highest use of elastomer blends is in the manufacture of tyres. Styrene/butadiene rubber (SBR) has better crack resistance, wet grip and weather resistance than natural rubber (NR), while NR has better strength and lower heat buildup than SBR and shows better performance at low temperature. Hence NR and SBR blends are used extensively in tyre manufacture.<sup>1</sup> The rubbers for tyre manufacture must have high elasticity and frictional properties as well as a high load bearing capacity. Conforming to these needs the rubbers are vulcanised under different conditions with various additives.

To obtain better end use properties, rubber is subjected to vulcanisation with different types and amounts of accelerators. The reactivity of sulphur during vulcanisation and the physical properties obtained are affected by the chemical structure, molecular weight and conformation of the elastomers. Sulphur vulcanisation with unsaturated rubbers occurs via complicated radical substitution in the form of mono, di, and polysulphide bridges and sulphur containing intracyclisation with the polymer molecules. The density

and distribution of crosslinks affect the physical properties and the stability on aging; they are dependent on the accelerator type, the ratio of accelerator to sulphur, reaction temperature, and time. The rate of vulcanisation in SBR is slower than in NR owing to its less unsaturated nature and the non-linearity of the molecular structure. This retardation could be overcome by the use of binary accelerators.

Binary accelerator systems enhance the efficiency of sulphur uptake during crosslinking, which in turn improves the mechanical properties of finished rubber goods. Owing to the reduced time required for curing and the production of better end use products, the study of new accelerator systems remains a major research topic.<sup>2–5</sup> Although the mechanism of vulcanisation is still open for debate, the use of different curatives has gained importance depending on their performance. The synergistic behaviour of these systems is said to be due to the formation of new chemical moieties, which make the curing process easier. The objective of the present study was to evaluate the effect of a new binary system based on 1-phenyl-2,4-dithiobiuret (DTB), and sulphenamides such as dicyclohexyl benzothiazyl sulphenamide (DCBS), tertiary butyl benzothiazole sulphenamide (TBBS) and morpholinothio benzothiazole sulphenamide (MBS) in NR–SBR blends. The study concentrates on processing, mechanical, and network characteristics.



1 Reaction scheme showing preparation of 1-phenyl-2,4-dithiobiuret

**EXPERIMENTAL**

**Materials**

The NR used was ISNR-5 obtained from the Rubber Research Institute of India. The SBR used was Synaprene-1502 with a 25% styrene content (made by the emulsion process) supplied by Synthetic and Chemicals Ltd, India. The curatives zinc oxide, stearic acid and sulphur were commercial grade obtained from Ranbaxy, India. Accelerators such as DCBS, TBBS and MBS were obtained from Bayer AG, Germany. The DTB was synthesised based on the procedure given below. Propane thiol, piperidine etc. were of analytical reagent grade supplied by E-Merck, Germany.

**Preparation of 1-phenyl-2,4-dithiobiuret**

Phenyl isothiocyanate, obtained by steam distillation of ammonium phenyl dithiocarbamate with lead nitrate, was added dropwise into a stirred solution of thiourea and powdered sodium hydroxide in acetonitrile, and the reaction mixture was heated. A clear solution resulted, which was then diluted with water and later acidified with concentrated hydrochloric acid. The crude 1-phenyl-2,4-dithiobiuret precipitate obtained was dissolved in a minimum quantity of aqueous sodium hydroxide and then filtered. The alkaline filtrate on acidification again yielded the 1-phenyl-2,4-dithiobiuret precipitate, which was recrystallised from ethanol. The sequence of reactions is given in Fig. 1.

**Preparation of vulcanisates**

Compounding of NR-SBR blends was carried out on a two roll open mill according to ASTM D 16 627. The formulations of the mixes are given in Table 1. The rheographs of the mixes and their cure characteristics were obtained using a Monsanto rheometer model R-100. The mixes were cured in a hydraulic press at 150°C for the optimum cure time  $t_{90}$ , which is defined as the time required for obtaining the torque  $T_{90}$ , which is given by

$$T_{90} = \frac{90(M_H - M_L)}{100} + M_L \dots \dots \dots (1)$$

where  $M_H$  is the maximum torque and  $M_L$  is the minimum torque.

**Mechanical properties**

The tensile properties and tear resistance of the compounds were measured on an Instron tensile testing machine at a crosshead speed of 500 mm min<sup>-1</sup> according to ASTM D 412:98a and ASTM D 624:98, respectively.

The hardness of the cured compound was measured according to ASTM D 2240:97 using a Shore A type durometer. Compression set of the compounds was measured according to ASTM D 396:98. The thermal aging of the samples was carried out in an aging oven at 70°C for 24 h according to ASTM D 572:99. The resilience of the samples was measured using a Dunlop triposometer according to ASTM D 2632:96.

**Swelling measurements**

A testpiece weighing ~0.2 g was cut from the compression moulded rubber sample. The sample was immersed in pure toluene at room temperature to allow the swelling to reach diffusion equilibrium.<sup>6</sup> At the end of this period the testpiece was taken out, the adhering liquid was rapidly removed by blotting with filter paper and the swollen weight was immediately measured. The samples were dried in vacuum to constant weight and the desorbed weight was measured. The swelling ratio is defined as

$$R = (W_1 - W_0) / W_0 \dots \dots \dots (2)$$

where  $W_0$  is the weight of the testpiece before swelling and  $W_1$  is the weight of the swollen testpiece after time  $t$  of immersion. The swelling ratio is a direct measurement of the degree of crosslinking – the smaller the ratio, the higher the degree of crosslinking.

Table 1 Cure characteristics of mixes (EV)\*

Code	DTB, phr	Accelerator, 1.5 phr	Max. torque, d Nm	Min. torque, d Nm	Scorch time $t_{10}$ , min	Optimum cure time $t_{90}$ , min	Cure rate index, min <sup>-1</sup>
P <sub>0</sub>	0	DCBS	29.9	3.8	25.6	48.2	2.89
P <sub>1</sub>	0.5	DCBS	30.1	3.6	10.5	24.8	4.92
P <sub>2</sub>	1.5	DCBS	32.8	4.5	3.8	19.25	6.07
Q <sub>0</sub>	0	TBBS	38.4	3.8	22.2	42.6	4.9
Q <sub>1</sub>	0.5	TBBS	40.7	3.7	4.3	23.5	5.21
Q <sub>2</sub>	1.5	TBBS	42.8	3.7	2.4	16.8	9.61
R <sub>0</sub>	0	MBS	33.9	3.5	23.8	42.3	5.41
R <sub>1</sub>	0.5	MBS	34.4	3.3	7.6	18.8	8.92
R <sub>2</sub>	1.5	MBS	39.8	4.4	1.9	10.7	11.36

\* Stock composition: NR-SBR (50:50), 100 g; zinc oxide, 5 phr; stearic acid, 2 phr; sulphur, 0.5 phr.

The concentration of crosslinks was determined using the equilibrium swelling data.<sup>7</sup> The volume fraction of rubber  $V_r$  in the swollen network was then calculated by the method reported by Ellis and Welding.<sup>8</sup> The crosslink density was determined using the Flory-Rehner theory.<sup>9</sup>

$$M_c = \frac{-\rho_p V_s (V_r)^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2} \dots \dots \dots (3)$$

where  $V_s$  is the molar volume of the solvent and  $\chi$  the interaction parameter. For the NR-toluene system,  $\chi$  can be taken as a constant (0.43).<sup>10</sup> For the SBR-toluene system,  $\chi$  is given by<sup>11</sup>

$$\chi = 0.330 + 0.43 V_r \dots \dots \dots (4)$$

Crosslink density is calculated using

$$v = 1/2M_c \dots \dots \dots (5)$$

The concentration of polysulphidic crosslinks was estimated from the change in the crosslink density of the vulcanisates before and after treatment with propane-2-thiol and piperidine, which cleaves only the polysulphidic crosslinks.<sup>12</sup> Both polysulphidic and disulphidic crosslinks in the vulcanisates can be cleaved by treatment with 1-hexane thiol in piperidine. The determination of crosslink density before and after this treatment gives the concentration of monosulphidic linkages, assuming the number of carbon-carbon linkages formed during vulcanisation is negligible.<sup>13</sup> Since the samples were difficult to handle after the treatment with 1-hexanethiol, the concentrations of mono and disulphidic linkages are reported together.

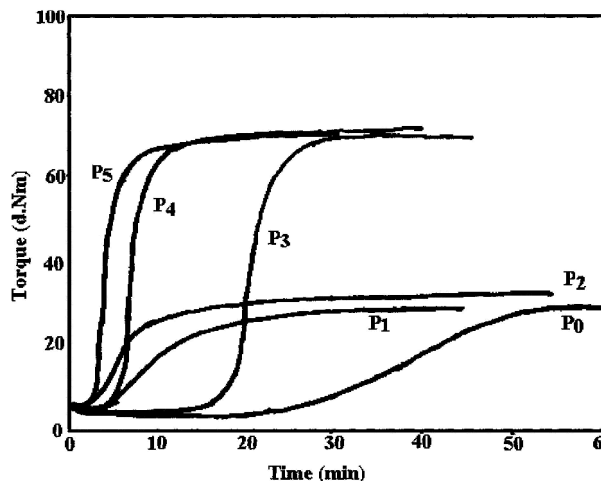
**Dynamic mechanical measurements**

Dynamic mechanical thermal analysis (DMTA) was carried out on an Eplexor™ 150 N instrument (Gabo Qualimeter, Ahlden, Germany). Viscoelastic material parameters such as storage modulus  $E'$ , mechanical loss factor  $\tan \delta$  and loss modulus  $E''$  were measured over a broad temperature range (-110 to +60°C) at a heating rate of 0.8 K min<sup>-1</sup>. Rectangular specimens of length 60 mm, width 10 mm and thickness 6 mm were subjected to tensile loading at a frequency of 10 Hz.

**RESULTS AND DISCUSSION**

**Cure characteristics**

In the present study NR-SBR (50:50) blends were vulcanised with two different vulcanisation systems, i.e. the efficient and the conventional. The difference



suffixes 0, 1, and 2 indicate DTB concentrations of 0, 0.5 and 1.5 phr, respectively, (EV); suffixes 3, 4, 5, indicate DTB concentrations of 0, 0.4 and 0.8 phr, respectively, (CV)

**2 Rheographs of NR-SBR mixes cured with DTB-DCBS accelerator system**

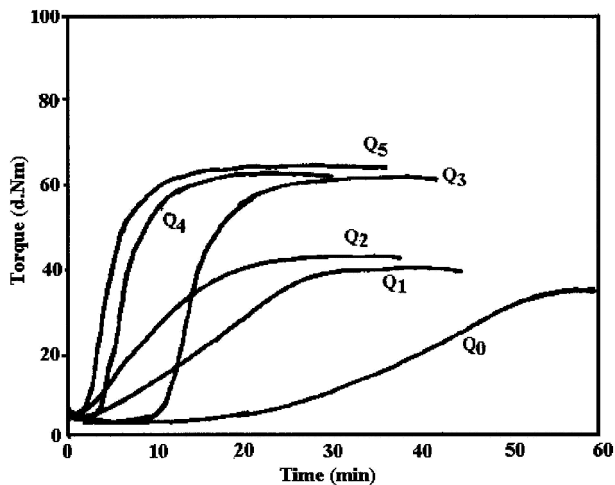
between the two systems is that, when the cure system is efficient (EV) the majority of crosslinks are mono and disulphidic, and when the cure system is conventional most are polysulphidic linkages.<sup>14</sup> Rheographs of the mixes are given in Figs. 2-4. The mixes P correspond to the DCBS system, Q to the TBBS system and R to the MBS system. To reduce the number of samples, only three loadings of DTB were selected for each system. In all the cases the suffixes 0, 1, and 2 indicate DTB concentrations of 0, 0.5 and 1.5 phr, respectively, (EV) and suffixes 3, 4, 5, indicate DTB concentrations of 0, 0.4 and 0.8, respectively, (CV). The minimum torque in the rheograph can be taken as a measure of the viscosity of the masticated rubber. Whenever there is excessive mastication, the viscosity registers a sharp decrease. Normally the maximum torque in the rheograph can be taken as the maximum viscosity of the rubber compound and is an approximate measure of the crosslink density in the sample.

The cure characteristics are given in Tables 1 and 2. The maximum torque, which is a measure of the stiffness of the compound, is found to increase with DTB concentration. It is directly related to the modulus of the compound. The cure activating nature of DTB in NR-SBR blends is evident from the processing characteristics of the vulcanisates. It is seen that as the concentration of DTB increases the time needed

**Table 2 Cure characteristics of mixes (CV)\***

Code	DTB, phr	Accelerator, 0.8 phr	Max. torque, d Nm	Min. torque, d Nm	Scorch time t <sub>10</sub> , min	Optimum cure time t <sub>90</sub> , min	Cure rate index, min <sup>-1</sup>
P <sub>3</sub>	0	DCBS	70.9	3.4	15.7	27.4	15.04
P <sub>4</sub>	0.4	DCBS	72	3.4	6.9	13.4	18.18
P <sub>5</sub>	0.8	DCBS	71.5	3.7	2.8	7.6	20.8
Q <sub>3</sub>	0	TBBS	61.6	2.7	10.3	20.1	10.2
Q <sub>4</sub>	0.4	TBBS	62.9	3.21	3.7	11.6	12.7
Q <sub>5</sub>	0.8	TBBS	63.9	4.45	2	9.17	13.95
R <sub>3</sub>	0	MBS	60	3.86	13.5	26.6	7.63
R <sub>4</sub>	0.4	MBS	60.4	3.6	4.2	12.2	12.5
R <sub>5</sub>	0.8	MBS	61.1	3.6	3.1	8.3	18.2

\* Stock composition: NR-SBR (50:50), 100 g; zinc oxide, 5 phr; stearic acid, 2 phr; sulphur, 2.5 phr.



suffices 0, 1, and 2 indicate DTB concentrations of 0, 0.5 and 1.5 phr, respectively, (EV); suffices 3, 4, 5, indicate DTB concentrations of 0, 0.4 and 0.8 phr, respectively, (CV)

**3 Rheographs of NR-SBR mixes cured with DTB-TBBS accelerator system**

for optimum cure  $t_{90}$  decreases. The decrease in cure time is extremely beneficial because it increases the production rate. However the scorch time is also decreasing. This affects the scorch safety of the compound. It is seen that sulphenamides show a longer scorch time. The relative order of scorch delay varies with the type of the stock, especially with the ratio of accelerator to sulphur.

When DTB is added as a secondary accelerator it is seen that DCBS shows better scorch delay, followed by TBBS and MBS. In all cases addition of DTB decreases scorch time. The delayed action of sulphenamides can be explained by the assumption that intermediates are formed through the reaction of sulphenamides with activated sulphur and when these intermediates are stable, the reaction of rubber with activated sulphur is delayed. The DTB activated the reaction with all the three sulphenamides, which indicates a lower stability of the intermediates.

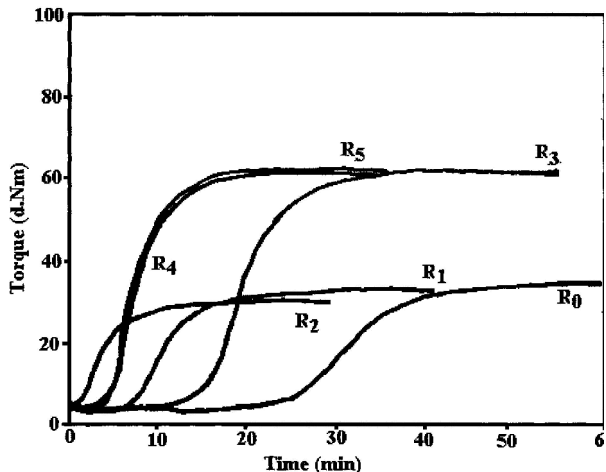
**Kinetic studies**

The cure rate index (CRI) value, which is a measure of the rate of the vulcanisation process, is given by

$$CRI = 100/(t_{90} - t_{10}) \dots \dots \dots (6)$$

It is seen from Tables 1 and 2 that the CRI of the mixes increases significantly with DTB dosage. As more DTB is used, its effects on the CRI are greater in the EV system than in the CV system. This further indicates the cure activating nature of the secondary accelerator DTB.

It is well known that accelerated sulphur vulcanisation in rubbers proceeds via the formation of an active sulphurating agent. Even if sulphur is added as the crosslinking agent, the actual sulphurating agent, formed by the reaction of accelerator, sulphur and activators, is a zinc perthiomercaptide complex. It is this complex that breaks the Zn-S bonds and makes linkages with the rubber hydrocarbon. When DTB is added as the binary accelerator, owing to its nucleophilicity the C-S bond becomes polarised and weakens. The C-S bond breaks. This breakaway



suffices 0, 1, and 2 indicate DTB concentrations of 0, 0.5 and 1.5 phr, respectively, (EV); suffices 3, 4, 5, indicate DTB concentrations of 0, 0.4 and 0.8 phr, respectively, (CV)

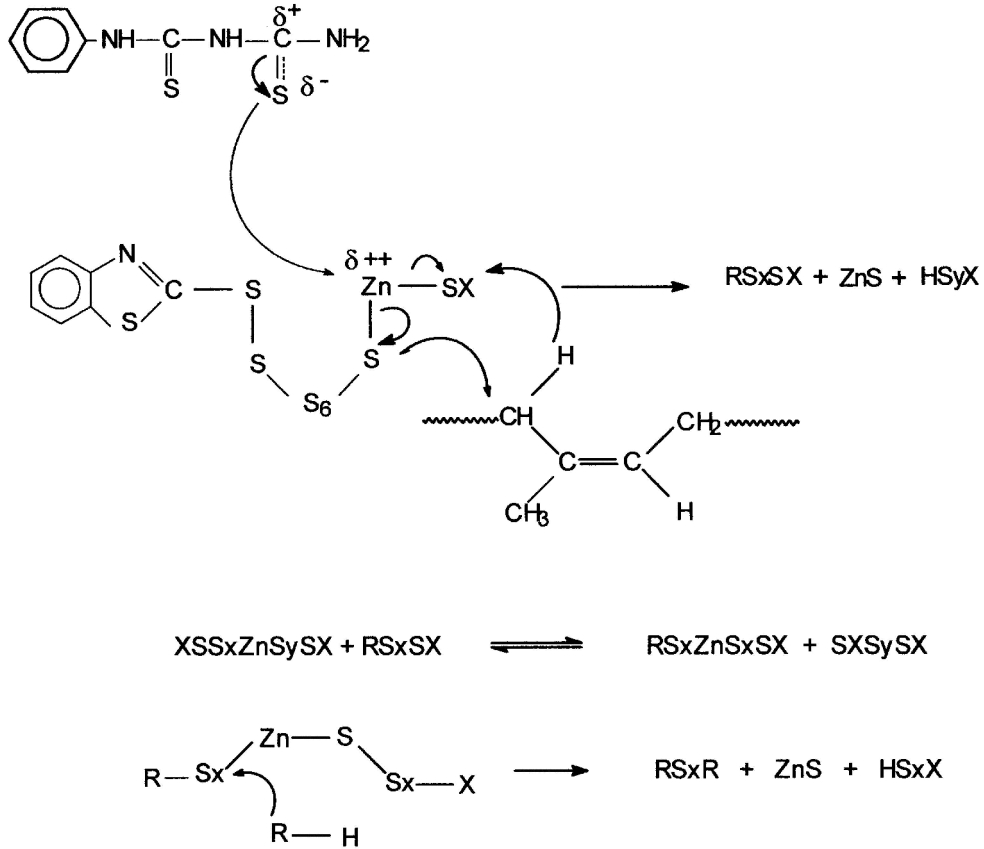
**4 Rheographs of NR-SBR mixes cured with DTB-MBS accelerator system**

sulphur attacks the Zn of the zincperthio salt. This helps the easy fracture of the Zn-S bond in the perthiosalt. The proposed reaction scheme, using NR as the hydrocarbon, is given in Fig. 5.

**Mechanical properties**

The stress-strain graphs of the samples cured via EV and CV systems are given in Figs. 6 and 7, respectively. In the EV curing system, the mixes cured with the primary accelerator alone show low strength and modulus. Strain induced crystallisation of NR is observed from the stress-strain curves. In addition, the elongation at break for the mixes cured with sulphenamides alone is higher. This indicates lower crosslink density. All other mixes show similar behaviour even if the primary accelerator is different. This indicates similar mechanisms operating in all these cases. A moderate strength compared with the NR vulcanisate is shown by 50:50 NR-SBR blends. The ability of DTB to impart more strength to the vulcanisates is clear from the graph. The toughness of the material also increased with DTB addition. This can be explained on the basis of increased crosslink density, which is discussed below. The CV compounds show similar behaviour. In CV systems, the blends show better strength and modulus than EV systems. The ability of DTB to impart better modulus and strength is clear. The elongation at break is less for the DTB cured samples. This indicates an improvement in crosslink density. The improved strength usually depends on the relative proportion of the crosslinks, which is discussed below.

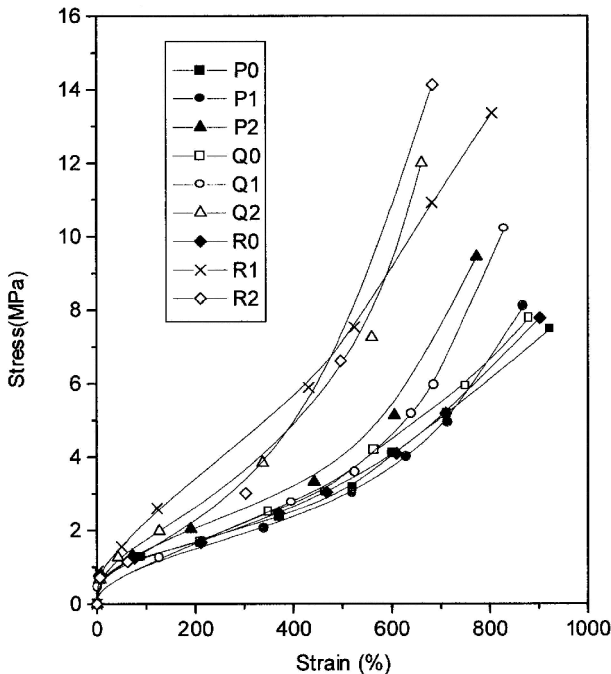
The mechanical properties of the vulcanisates are given in Tables 3 and 4. It is clear from the tables that the tensile strength increases slightly upon the first addition of DTB. As the concentration of DTB is increased to 1.5 phr, strength is further increased. This might be due to the increased crosslinking. In previous studies with NR, an optimum loading of DTB was observed for optimum properties.<sup>2,5</sup> In this case no optimum is shown within 1.5 phr of DTB. Owing to its lower level of unsaturation, SBR requires



**5 Proposed mechanism showing effect of DTB**

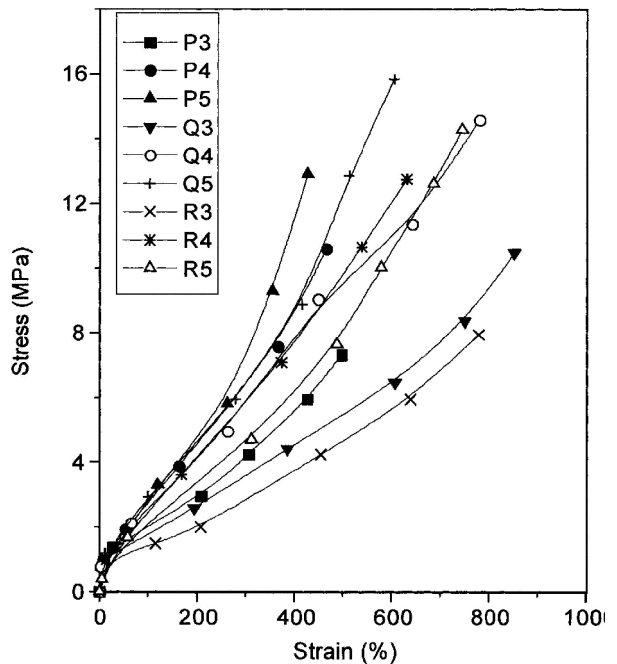
more accelerators to attain satisfactory crosslinking. Tear strength also increases with DTB addition. The higher strength is shown by the CV samples, which may be due to the better strength shown by the

polysulphidic linkages present in the CV samples. The modulus values at 300% elongation obtained for the NR-SBR blends are also given. It is clear from the table and the stress-strain curves that the modulus



P = DCBS system; Q = TBBS system; R = MBS system; suffixes as for Figs. 2-4

**6 Stress-strain graphs of NR-SBR vulcanisates (EV system)**



P = DCBS system; Q = TBBS system; R = MBS system; suffixes as for Figs. 2-4

**7 Stress-strain graphs of NR-SBR vulcanisates (CV system)**

**Table 3 Mechanical properties of NR-SBR vulcanisates (EV)**

Mix	Tensile strength, MPa	Tear strength, N mm <sup>-1</sup>	Elongation at break, %	Modulus at 300% elongation, MPa	Hardness, Shore A	Resilience, %
P <sub>0</sub>	7.46	9.63	922	2.10	35	24
P <sub>1</sub>	8.08	10.85	867	2.20	40	25
P <sub>2</sub>	9.44	11.2	773	2.60	42	25
Q <sub>0</sub>	7.94	8.56	950	2.21	38	22
Q <sub>1</sub>	10.2	10.32	742	2.29	43	22
Q <sub>2</sub>	12.16	10.5	626	3.41	43	23
R <sub>0</sub>	8.07	8.7	896	2.11	34	21
R <sub>1</sub>	13.3	12.4	824	3.64	41	23
R <sub>2</sub>	14.48	12.85	603	3.32	45	24

**Table 4 Mechanical properties of NR-SBR vulcanisates (CV)**

Mix	Tensile strength, MPa	Tear strength, N mm <sup>-1</sup>	Elongation at break, %	Modulus at 300% elongation, MPa	Hardness, Shore A	Resilience, %
P <sub>3</sub>	7.31	12.35	497	4.11	40	29
P <sub>4</sub>	10.59	15.2	466	6.46	44	29
P <sub>5</sub>	12.94	16.8	428	7.3	46	30
Q <sub>3</sub>	10.54	11.54	898	3.61	39	27
Q <sub>4</sub>	14.59	16.24	780	5.84	41	28
Q <sub>5</sub>	15.93	15.9	605	6.46	44	29
R <sub>3</sub>	7.94	12.3	779	2.82	41	27
R <sub>4</sub>	12.28	14.5	646	5.84	46	28
R <sub>5</sub>	13.56	16.2	686	4.73	48	28

values of DTB cured samples are high. This may be due to an increase in crosslink density of the samples. For the MBS cured samples a decrease in modulus is observed upon addition of 1.5 phr DTB. This may be due to the low amount of polysulphidic linkages. Service properties such as hardness and resilience show little change with DTB. Conventionally cured samples show an improvement in both hardness and resilience. This may be due to the predominance of polysulphidic linkages in the CV system.

### Network characterisation

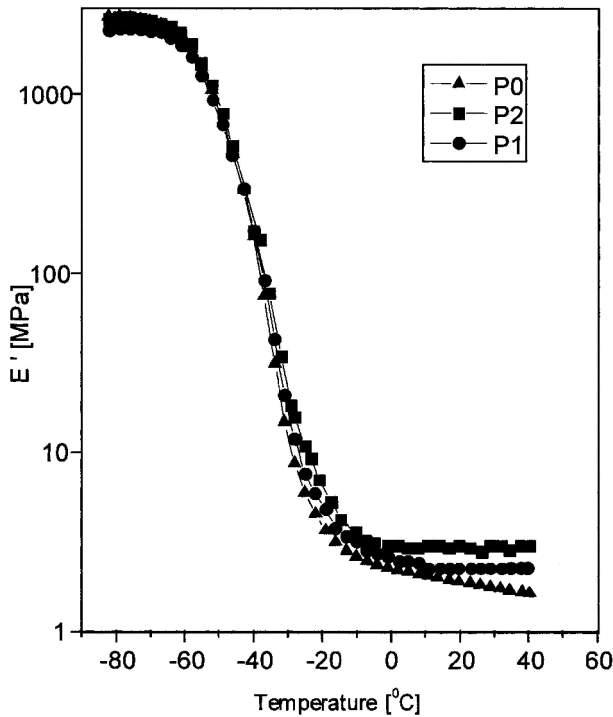
Swelling was measured to calculate the crosslink density. The calculated values of the crosslink densities are given in Tables 5 and 6. The relative proportions of crosslinks were estimated by the thiol treatment detailed above. In the EV system, the crosslink density increased with DTB addition. The number of polysulphidic linkages is at a minimum, in contrast to the mono and disulphidic linkages, which is supported by previous evidence. It is seen that as the amount of

**Table 5 Network characteristics of NR-SBR vulcanisates (EV)**

Mix	Net chemical crosslink density $\nu \times 10^5$ , mol g <sup>-1</sup>	Mono and disulphidic linkages $\nu \times 10^5$ , mol g <sup>-1</sup>	Polysulphidic linkages $\nu \times 10^5$ , mol g <sup>-1</sup>	Swelling ratio
P <sub>0</sub>	1.216	0.6698	0.5462	7.699
P <sub>1</sub>	1.265	0.7321	0.4329	6.071
P <sub>2</sub>	1.4289	0.8076	0.6213	5.935
Q <sub>0</sub>	1.1324	0.7792	0.6532	7.425
Q <sub>1</sub>	1.583	0.8119	0.7051	6.063
Q <sub>2</sub>	1.965	1.296	0.7234	5.772
R <sub>0</sub>	1.194	0.7429	0.4511	7.653
R <sub>1</sub>	1.825	1.156	0.7685	6.025
R <sub>2</sub>	1.848	1.221	0.6213	6.851

**Table 6 Network characteristics of NR-SBR vulcanisates (CV)**

Mix	Net chemical crosslink density $\nu \times 10^5$ , mol g <sup>-1</sup>	Mono and disulphidic linkages $\nu \times 10^5$ , mol g <sup>-1</sup>	Polysulphidic linkages $\nu \times 10^5$ , mol g <sup>-1</sup>	Swelling ratio
P <sub>3</sub>	3.01	1.097	1.913	3.313
P <sub>4</sub>	4.55	1.23	3.32	3.246
P <sub>5</sub>	4.94	1.3	3.61	3.162
Q <sub>3</sub>	3.89	1.12	2.54	3.907
Q <sub>4</sub>	4.915	1.73	3.21	3.781
Q <sub>5</sub>	5.65	1.86	3.76	3.582
R <sub>3</sub>	3.443	1.147	2.295	7.235
R <sub>4</sub>	5.379	1.73	3.845	3.872
R <sub>5</sub>	5.575	1.608	3.751	4.188



suffixes 0, 1, and 2 indicate DTB concentrations of 0, 0.5 and 1.5 phr, respectively, (EV)

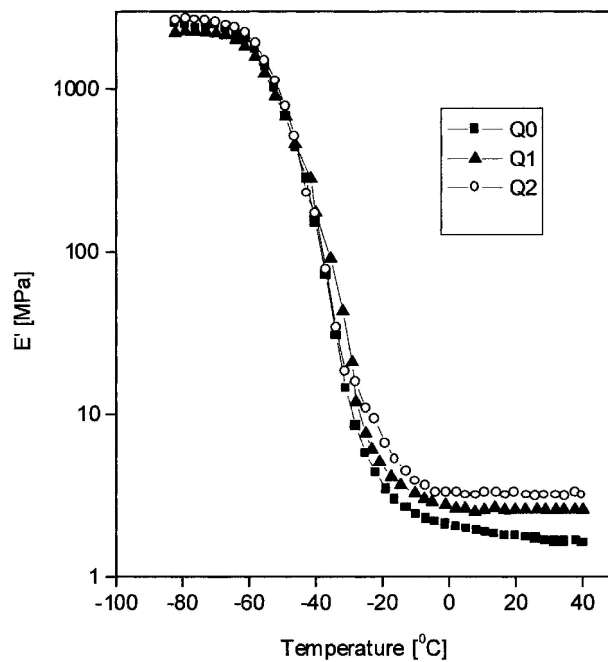
**8 Variation of storage modulus with temperature for vulcanisates cured with DCBS-DTB system**

DTB increases the number of polysulphidic linkages also tends to increase. The behaviour is less consistent in the EV system but more prominent in the CV system. This gives an indication of the ability of DTB to form polysulphidic linkages. The DTB is found to be nucleophilic in nature, making the breakage of the Zn-S bond in the zinc perthiomercaptide complexes easier, and thereby helping bond formation with the rubber hydrocarbon (see Fig. 5).

In the CV system, higher dosages of DTB produce maximum values of crosslink density. In this case the numbers of polysulphidic linkages are higher than mono and disulphidic linkages.

**Dynamic mechanical properties**

The storage modulus  $E'$  for different mixes cured with DTB-DCBS, DTB-TBBS and DTB-MBS over a wide range of temperature is plotted in Figs. 8-10, respectively. The curves for all the mixes have three



suffixes 0, 1, and 2 indicate DTB concentrations of 0, 0.5 and 1.5 phr, respectively, (EV)

**9 Variation of storage modulus with temperature for vulcanisates cured with TBBS-DTB system**

distinct regions: glassy; leathery (transition); and rubbery. The storage modulus decreases sharply with increase in temperature. It is seen that the storage modulus in the glassy region is lower for DTB cured vulcanisates. For the MBS-DTB system an irregularity is observed in the modulus in the glassy region. In the glassy state, long range molecular motions are stopped. The storage modulus in the rubbery region is an indication of entanglement density, which is discussed below.

The glass transition temperatures of the vulcanisates found from the loss tangent curves and loss modulus curves are given in Table 7. It is observed that the glass transition values of the NR and SBR phases are close to each other. This is because the  $T_g$ s of pure NR and SBR differ only by 20 K. For small differences in  $T_g$ , usually the peaks of individual polymers merge. A shift in  $T_g$  is observed with DTB addition for the two phases, which represents crosslinking. A higher  $T_g$  is observed for DTB cured vulcanisates. The observations are similar for all three systems,

**Table 7 Viscoelastic measurements of NR-SBR vulcanisates**

Mix	Entanglement density $\nu \times 10^5, \text{ mol m}^{-3}$	$T_g$ (SBR phase)		$T_g$ (NR phase)	
		Loss tangent curves	Loss modulus curves	Loss tangent curves	Loss modulus curves
P <sub>0</sub>	1.249	-32.96	-43.29	-46.07	-55.79
P <sub>1</sub>	1.604	-30.96	-42.69	-46.07	-55.2
P <sub>2</sub>	1.95	-29.98	-39.12	-46.66	-58.77
Q <sub>0</sub>	1.25	-33.05	-44.24	-51.81	-59.67
Q <sub>1</sub>	1.857	-31.71	-43.15	-49.80	-59.5
Q <sub>2</sub>	2.178	-31.04	-42.79	-46.45	-58.35
R <sub>0</sub>	1.97	-36.5	-41.2	-51.5	-60.61
R <sub>1</sub>	2.48	-34.15	-40.55	-50.24	-60.11
R <sub>2</sub>	3.46	-31.17	-39.66	-49.05	-55.64

indicating a similar mechanism operating for DTB and the sulphenamides in the curing of NR-SBR blends.

The viscoelastic properties of polymers are markedly dependent on the type of crosslinks and the degree of crosslinking. The storage modulus in the rubbery plateau region increases with increase in crosslink density (entanglement density). The modulus in the rubbery region was used to determine the crosslink density of rubber materials in accordance with rubber elasticity theories. According to the statistical theory of rubber elasticity, the crosslink density  $\nu$  for a tetra-functional network can be calculated according to the equation<sup>17</sup>

$$\nu = E'/6dRT \quad \dots \quad (7)$$

where  $E'$  is the dynamic storage modulus measured from the rubbery plateau region,  $d$  is the density of the vulcanisate,  $R$  is the universal gas constant and  $T$  is the absolute temperature. The entanglement density values are given in Table 7. The entanglement density calculated from the modulus measurement increased with addition of DTB. This is in accordance with the observed crosslink density value from the swelling measurements. Higher entanglement density is shown by vulcanisates with higher amounts of DTB. Thus it is confirmed from modulus studies that DTB assists crosslink formation either by sulphur donation or by favouring the formation of intermediates. The trends in entanglement density observed with DTB addition by vulcanisates cured with DCBS, TBBS and MBS are similar. Thus it is also confirmed that the effect of DTB upon different sulphenamides is similar irrespective of the ligand, and this supports the proposed mechanism.

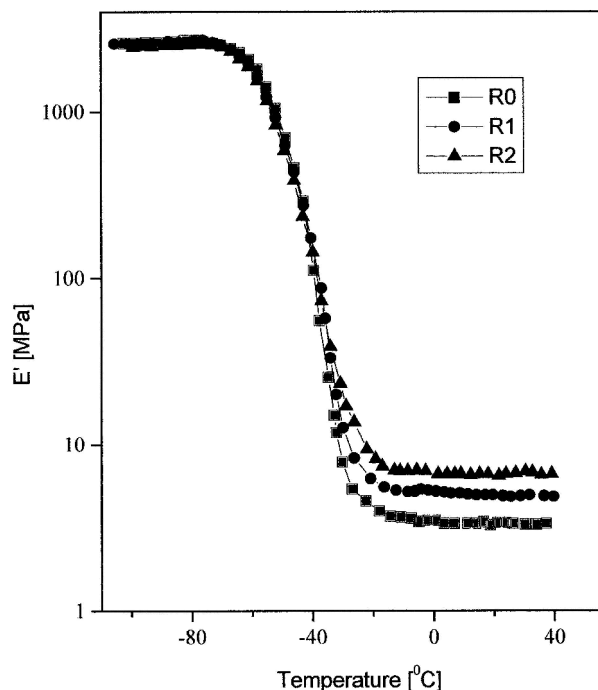
## CONCLUSIONS

The effect of 1-phenyl-2,4-dithiobiuret as a secondary accelerator with sulphenamides in natural rubber-styrene/buadiene rubber blends has been studied in detail. Based on the cure characteristics it is seen that DTB is able to activate cure in NR-SBR blends. Irrespective of the ligands, DTB activates the curing process with sulphenamides in efficiently and conventionally cured NR-SBR blends. Better mechanical properties were also obtained for DTB cured vulcanisates. No optimum concentration for DTB was found within 1.5 phr of DTB. Higher strength was obtained with higher loading of DTB. Based on these observations a possible mechanism for the cure activation with DTB is suggested.

Crosslink density of NR-SBR blends improved with addition of DTB indicating the ability of DTB to form more crosslinks either by sulphur donation or by favouring the formation of intermediates. Dynamic mechanical studies also indicated improved crosslinking with DTB. Based on these studies it is clear that DTB could be effectively used as a binary accelerator in vulcanisation of NR-SBR blends.

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suffixes 0, 1, and 2 indicate DTB concentrations of 0, 0.5 and 1.5 phr, respectively, (EV)

**10** Variation of storage modulus with temperature for vulcanisates cured with MBS-DTB system

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## REFERENCES

1. P. J. CORISH: in 'Polymer blends and mixtures', (ed. D. J. Walsh *et al.*), 245; 1985, Dordrecht, Martinus Nijhoff.
2. A. S. APREM, G. MATHEW, K. JOSEPH, and S. THOMAS: *J. Rubber Res.*, 2001, **4**, (1), 44.
3. P. K. DAS, R. N. DATTA, and D. K. BASU: *Rubber Chem. Technol.*, 1988, **61**, 760.
4. V. T. E. MINI, C. MATHEW, A. P. KURIAKOSE, and D. J. FRANCIS: *J. Mater. Sci.*, 1995, **3**, 2049.
5. A. S. APREM, G. MATHEW, G. MATHEW, K. JOSEPH, and S. THOMAS: *Kautsch. Gummi Kunstst.*, 1999, **59**, 576.
6. G. N. BYRAN and G. W. WELDING: *Tech. Polym. Sci.*, 1963, **17**, 75.
7. A. D. T. GORTON and T. D. PENDLE: *Nat. Rubber Technol.*, 1976, **7**, (4), 77.
8. B. ELLIS and G. W. WELDING: *Rubber Chem. Technol.*, 1964, **37**, 571.
9. P. J. FLORY and J. REHNER: *J. Chem. Phys.*, 1943, **11**, 5120.
10. G. KRAUS: *Rubber Chem. Technol.*, 1953, **30**, 928.
11. B. MEISSNER: 'Physical properties of polymers', Part 1; 1971, Prague.
12. D. S. CAMPBELL: *J. Polym. Sci. B, Polym. Phys.*, 1969, **13**, 120.
13. D. S. CAMPBELL and B. SAVILLE: Proc. Int. Rubber Conf., Brighton, 1967.
14. A. V. CHAPMAN and M. PORTER: 'Natural rubber science and technology', (ed. A. D. Roberts), Ch. 12; 1988, New York, Oxford Scientific Publications.
15. K. FUJIMOTO, T. NISHI, and T. OKAMOTO: *Int. Polym. Sci. Technol.*, 1981, **8**, (8), 30.
16. R. S. RIVLIN: *Rubber Chem. Technol.*, 1992, **65**, G51.
17. L. E. NIELSEN and L. E. LANDEL: 'Mechanical properties of polymers and composites', 2nd edn; 1994, New York, Marcel Dekker.