

Sulphur Vulcanisation of Styrene Butadiene Rubber using New Binary Accelerator Systems

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ABSTRACT: The influence of the newly developed binary accelerator 1-phenyl-2,4-dithiobiuret (DTB) in combination with sulphenamides like DCBS, MBS, TBBS on the cure characteristics, mechanical properties, viscoelastic behaviour and network characteristics of styrene butadiene rubber (SBR) is studied. Kinetics of vulcanisation is followed at three different temperatures. Mechanical properties are found to be improved upon DTB addition. Attempts have been made to correlate the observed properties with extent of crosslinking of DTB. Effect of aging on tensile properties of the vulcanisates was also done. The extent of crosslinking was also improved with DTB cured vulcanisates. Dynamic

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mechanical analysis has been done and the influence of the new accelerator systems on the modulus, glass transition and entanglement densities of the vulcanisates was investigated. The effect of fillers like carbon black and silica on DTB on technological properties of SBR vulcanisates and the extent of reinforcement caused by the fillers were also studied.

KEY WORDS: styrene butadiene rubber, vulcanisation, binary accelerator.

INTRODUCTION

IN THE PROCESS of vulcanisation a series of complex chemical reactions occur between the rubber, sulphur and auxiliary chemicals present, which change the soft and easily deformable raw rubber in to a strong and highly elastic material through the formation of crosslinks between the long chain molecules of the rubber. In the vulcanisation of diene rubbers using sulphur and accelerators, the efficiency of sulphur intake during crosslink formation is mainly dependent on the type of accelerator system, structure of the base polymer and temperature of vulcanisation.

Unlike natural rubber, in the vulcanisation of styrene butadiene rubber, a copolymer, the crosslink formation is relatively slower and therefore requires higher amounts of accelerator and lower levels of sulphur. This is attributed mainly to the lower number of double bonds, which are responsible for crosslinking with sulphur. The non-linear molecular structure in SBR is responsible for fewer crosslinking opportunities. In addition to this, the trace amount of resinous substances or fatty acids left over in the emulsion polymerised SBR could also contribute in retarding the process of vulcanisation. It is also known that gum SBR vulcanisates possess only a low strength, when compared to natural rubber. This inferiority in strength limits the importance of this synthetic material.

The retardation in curing could be overcome by the use of a combination of accelerators, which demand for increased production efficiency. Binary accelerator systems enhance the efficiency of sulphur intake during crosslinking, which in turn improves the mechanical, chemical and service properties of finished rubber goods. Besides these advantages binary accelerators are supposed to show excellent cure rate at lower temperatures. A majority of the properties depend on the type and amount of crosslinks formed in between the rubber hydrocarbon networks. The three essential features of the chemistry of a rubber network are (a) the number of crosslinks (b) the chemical structure of

these crosslinks and (c) the presence of non-crosslinking modifications to the polymer backbone. [1] In the present study attempts have been made to assess the contributions made by the first two of these factors to the vulcanisate performance.

The synthesis and use of a new compound (DTB) in natural rubber has been reported in our previous studies [2]. It has been found that DTB functions as a binary accelerator, which speeds up the cure reaction and improves the mechanical properties of NR vulcanisates. The present paper discusses the influence of this new binary accelerator 1-phenyl-2, 4-dithiobiuret on the sulphur vulcanisation of SBR. DTB was used with sulphenamides like MBS, DCBS, TBBS etc. in order to get a clear picture of cure activation with sulphenamides. Kinetics of the curing process was followed by studying the processing characteristics at different temperatures. Dynamic mechanical analysis of the vulcanisates can often be used to study the crosslinking in polymers. The dynamic mechanical properties, storage modulus (E'), loss modulus (E'') and loss factor ($\tan\delta$) of polymers depend on structure, crystallinity, extent of crosslinking etc.

It has been claimed [3] that there is no sulphur cure system at present, which yields satisfactory cure properties in combination with silica unless the chemical groups on the surfaces of the filler are modified additives such as organosilanes. The present study examined this claim with respect to the compounds loaded with silica. It has been noted that [4] SBR vulcanisates filled with silica show longer cure times and slower cure rates. In this work we have also tried to formulate an accelerated sulphur vulcanisation system for faster cure in silica filled SBR.

EXPERIMENTAL

Materials

Styrene butadiene rubber used was Synaprene-1502 with a 25% styrene content (made by emulsion process) supplied by Synthetic & Chemicals Ltd. Bareilly, UP, India. The curatives zinc oxide, stearic acid and sulphur, used was of commercial grade obtained from Ranbaxy Ltd. Bombay, India. Accelerators like DCBS, TBBS, and MBS was obtained from Bayer AG, Germany. DTB was synthesized based on the procedure given below. Propane-2-thiol, hexane-1-thiol, piperidine etc. were of analytical reagent grade supplied by E-Merck, Germany.

Preparation of 1-phenyl-2, 4-dithiobiuret

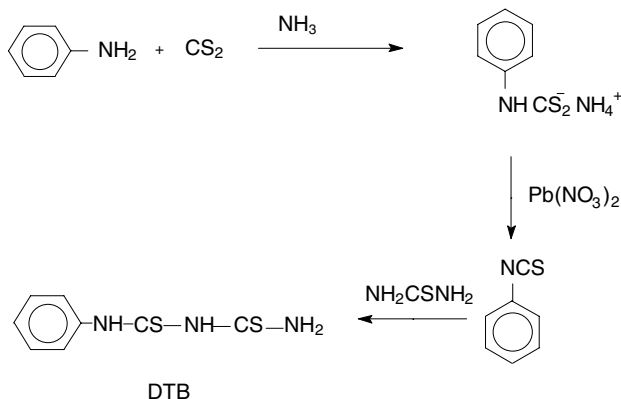
Phenyl isothiocyanate obtained by steam distillation of ammonium phenyl dithiocarbamate and lead nitrate was added dropwise into a stirred solution of thiourea and powdered sodium hydroxide in acetonitrile and the reaction mixture was heated. A clear solution resulted, which was then diluted with water and later acidified with concentrated hydrochloric acid. The crude 1-phenyl-2,4- dithiobiuret precipitate obtained was dissolved in 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 Scheme 1.

Preparation of Vulcanisates

Compounding of SBR was carried out on a two roll open mill according to ASTM-D-3182-94. The formulations of the mixes are given in Table 1. The rheograph of the mixes and their cure characteristics were obtained using Monsanto Rheometer R-100. The mixes were cured in a hydraulic press at 150°C for the optimum cure time.

Mechanical Properties

The tensile properties and tear resistance of the compounds was measured on an Instron tensile testing machine at a crosshead speed of



SCHEME 1.

Table 1. Composition of mixes.

	Mix Number								
	D0	D1	D2	E0	E1	E2	F0	F1	F2
Ingredients									
SBR	100	100	100	100	100	100	100	100	100
ZnO (phr)	5	5	5	5	5	5	5	5	5
Stearic acid (phr)	2	2	2	2	2	2	2	2	2
Accelerator (phr)	DCBS-1.5	DCBS-1.5	DCBS-1.5	TBBS-1.5	TBBS-1.5	TBBS-1.5	MBS-1.5	MBS-1.5	MBS-1.5
DTB (phr)	0	0.5	1.5	0	0.5	1.5	0	0.5	1.5
Sulphur (phr)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

500 mm/min 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 ageing oven at 70°C for 24 h as per ASTM D 572-99. The resilience of the samples was measured using a Dunlop Tripsometer according to ASTM D 2632-96.

Swelling Measurements

A test piece weighing about 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 [5]. At the end of this period, the test piece was taken out and the adhered 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 taken. The swelling ratio is defined as

$$R = (W_1 - W_0)/W_0 \quad (1)$$

where W_0 is the weight of the test piece before swelling and W_1 is the weight of the swollen test piece 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. The concentration of the crosslinks was determined using the equilibrium swelling data [6]. The volume fraction of rubber (V_r) in the swollen network was then

calculated by the method reported by Ellis and Welding [7] using the following equation,

$$V_r = (D\rho_p^{-1})/(D\rho_p^{-1} + A_0\rho_s^{-1}) \quad (2)$$

where D is the deswollen weight of the test specimen, A_0 is the weight of the solvent absorbed, ρ_p and ρ_s are the density of the polymer and solvent respectively. The crosslink density was determined using the Flory–Rehner equation [8].

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

where V_s is the molar volume of the solvent and χ the interaction parameter. For SBR, toluene system χ is given by [9],

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

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 [10]. Both polysulphidic and disulphidic crosslinks in the vulcanisates could 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 carbon–carbon linkages formed during vulcanisation to be negligible [11]. Since the samples were difficult to handle after the treatment with 1-hexanethiol, we report the concentrations of mono- and di-sulphidic linkages together.

Dynamic Mechanical Measurements

DMTA tests were conducted on an EplexorTM 150 N (Gabo Qualimeter, Ahlden, Germany). Viscoelastic material parameters such as mechanical loss factor, storage modulus and loss modulus ($\tan\delta$, E' and E'' respectively) were measured over a broad temperature range (-110 to $+60^\circ\text{C}$) at a heating rate of $0.8^\circ\text{C}/\text{min}$. Rectangular specimens $60\text{ mm} \times 10\text{ mm} \times 6\text{ mm}$ (length \times width \times thickness) were subjected to tensile loading at a frequency of 10 Hz .

RESULTS AND DISCUSSION

Processing Characteristics

The rheographs of the mixes with accelerator combinations like DCBS/DTB, TBBS/DTB and MBS/DTB obtained at 150°C are given in Figures 1–3 respectively. The concentration of DTB was varied from 0 to 1.5 phr in the mixes. 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 will register a sharp decrease. Normally the maximum torque in the rheograph can be taken as the maximum viscosity of the rubber compound and is roughly a measure of the crosslink density in the sample. The cure characteristics are given in Table 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 styrene butadiene rubber is evident from the processing characteristics of the vulcanisates. It is seen that as the concentration of DTB is increased, optimum cure time (t_{90}) is decreased. The decrease in cure time is extremely beneficial because it increases the production rate. However, the scorch time is found to be

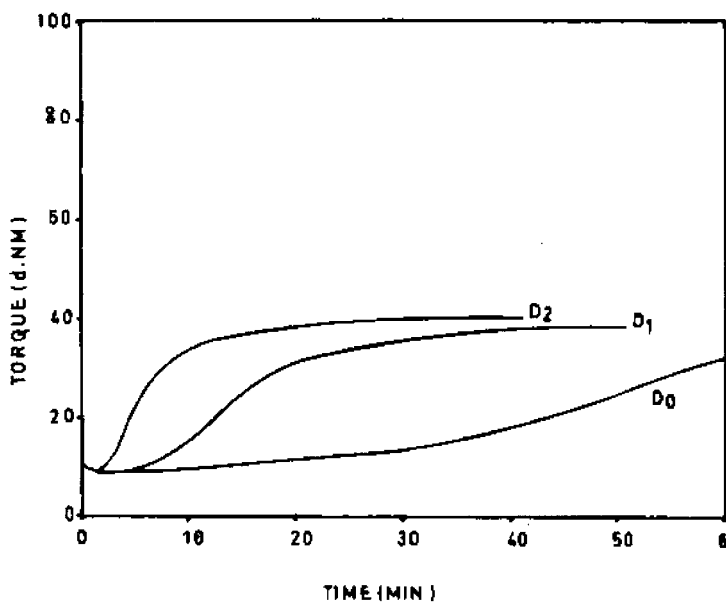


FIGURE 1. Rheograph of the DCBS/DTB mixes cured at 150°C.

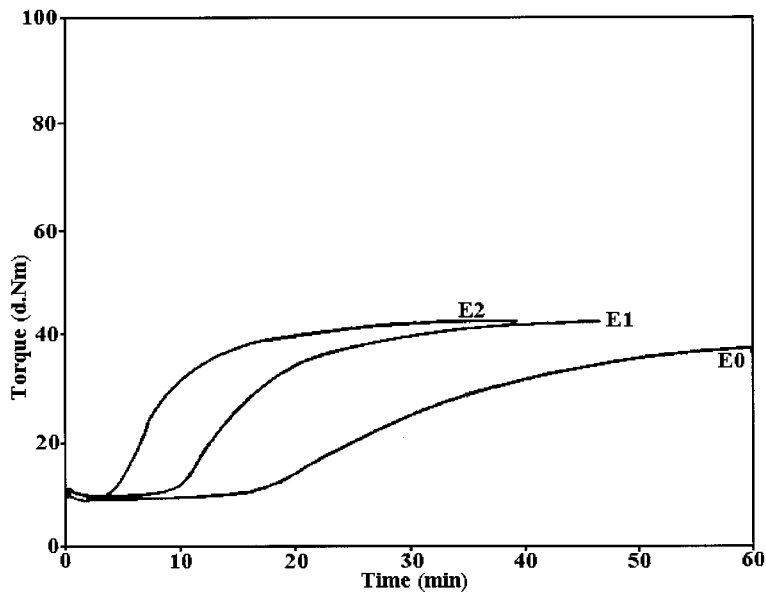


FIGURE 2. Rheograph of the TBBS/DTB mixes cured at 150°C.

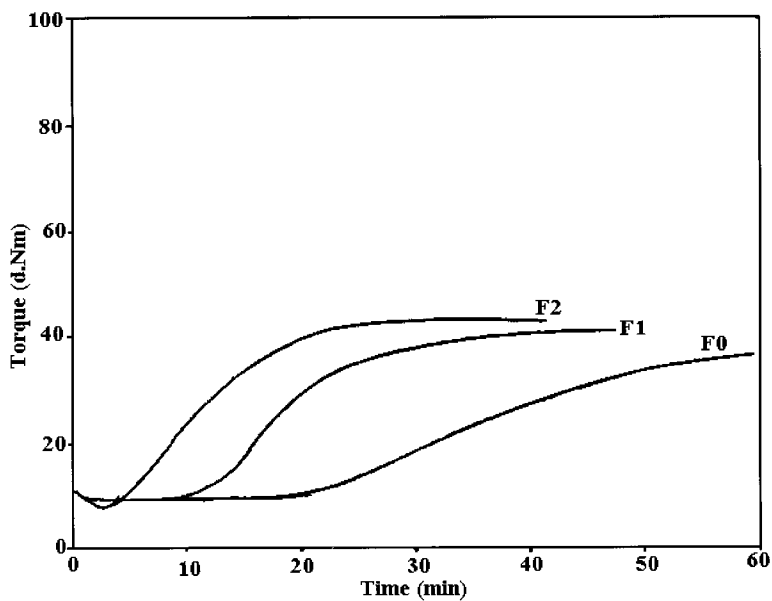


FIGURE 3. Rheograph of the MBS/DTB mixes cured at 150°C.

Table 2. Cure characteristics of gum vulcanisates.

	Mix Number								
	D0	D1	D2	E0	E1	E2	F0	F1	F2
Maximum torque (dNm)	31.86	38.64	40.24	34.9	42.1	42.5	36.45	41.19	42.5
Minimum torque (dNm)	8.6	8.8	8.9	8.9	8.9	8.8	8.82	8.7	8.8
Scorch time (min)	27.7	13.25	4.7	18.6	9.5	2.92	23.67	11.83	3.6
Optimum cure time (min)	56.25	29.8	16.3	47.3	28.5	18.9	51.4	31.17	15.2

decreasing. This in fact affects the scorch safety of the compound. Almost all the accelerators show a greater rate of decrease of scorch time with increasing temperature except some ultra fast accelerators.

Sulphenamides show a longer scorch time. Coran [4] proposed a slower rate of disappearance of the sulphenamide accelerator and its apparent immediate reaction product with sulphur in his kinetic scheme for the scorch delay of TBBS accelerator. TBBS dissociates into benzothiazoyl, sulphenyl, and amine radicals, polybenzothiazole which initiate the conversion of eight-membered sulphur ring to the active open chain sulphur. This contributes to (i) the greater scorch delays obtained by increasing the concentration of the heterolytic amine sulphenamide and (ii) the slower rate of acceleration shown by the sterically hindered amine sulphenamide. The relative order of scorch delay varies with the type of the stock, especially with the ratio of accelerator to sulphur. Morita and Young [5] have divided the sulphenamides into three groups according to the changes in scorch delay time, as the accelerator concentration is increase at constant sulphur level.

- (a) Scorch delay initially increases and then decreases (CBS, TBBS)
- (b) Scorch delay gradually increases (MBS)
- (c) Scorch delay decreases gradually (DCBS)

The scorch delay observed with sulphenamides vary in the order DCBS > MBS > TBBS. This is the normal observed trend with sulphenamide curing. The greater scorch time is shown by DCBS cured stocks followed by MBS and TBBS stocks. When DTB is added to the primary accelerator, scorch time decreased considerably indicating faster cure initiation by DTB. The variation in scorch time with temperature is shown in Figure 4. Mixes without DTB show the greater variation. When the amount of DTB is increased to 1.5 phr the decrease in scorch time with temperature decreased. This indicates the resistance of DTB towards reduction in scorch time with an increase in temperature.

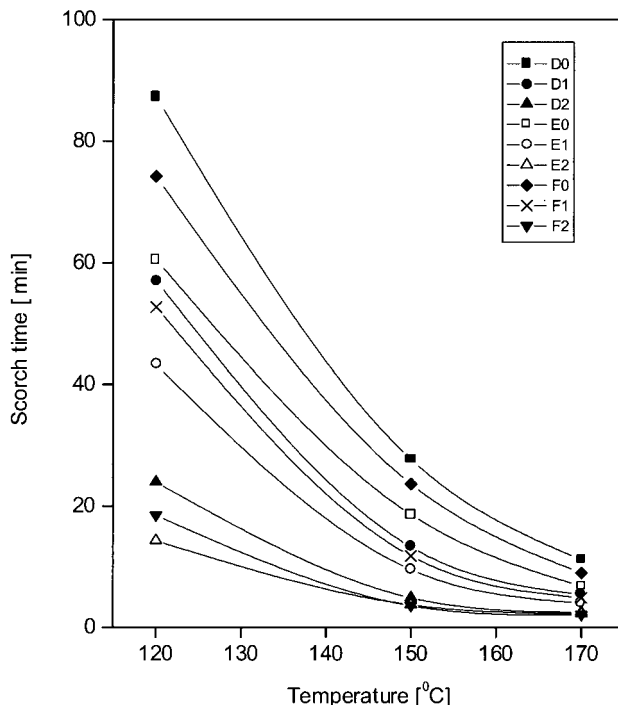


FIGURE 4. Scorch time of the mixes cured at different temperatures.

Kinetic Studies

The cure rate index (CRI) value, which is a measure of the rate of the vulcanisation process, increases significantly with DTB dosage. This further indicates the cure activating nature of the secondary accelerator DTB. The kinetics of vulcanisation was studied by the method reported by Fujimoto [12]. The general equation for the kinetics of a first order chemical reaction can be written as

$$\ln(a - x) = -kt + \ln a \quad (5)$$

where 'a' is the initial reactant concentration and 'x' is the reacted quantity of reactant at time 't' and 'k' is the first order rate constant. For the vulcanisation reaction of NR, the rate of crosslink formation is usually monitored by measuring the torque developed during vulcanisation. The torque values so obtained are proportional to the modulus of

the rubber. Since modulus and torque are analogous, we can substitute the torque value for modulus

$$(a - x) = M_h - M_t \quad (8)$$

$$a = M_h - M_n \quad (9)$$

where M_h , M_n , M_t are the maximum torque, minimum torque and torque at time t respectively. When $\ln(M_h - M_t)$ is plotted against time t , a straight-line graph is obtained as shown in Figure 5 which proves that the cure reaction follow first order kinetics. Even though linearity is claimed for the plots theoretically, deviations from linearity are experimentally observed for certain points. The observed linearity in the plots confirm that the cure reaction of the samples follow first order kinetics. It is also clear from the figure that a change in temperature does not affect the kinetic order of vulcanisation reaction. Similar graphs obtained for other accelerator combinations are avoided for simplicity. Regardless of temperature and concentration of DTB, all vulcanisation reactions proceed according to first order kinetics. The cure reaction rate constant values, k is obtained from the slope of the

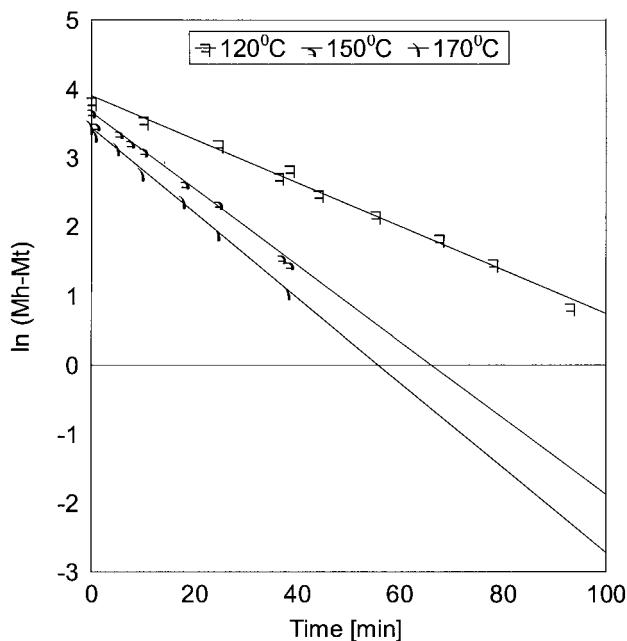


FIGURE 5. Kinetic plots of DTB added mixes.

respective straight lines. These values increase with temperature. It is also noted that the increase in k -values with temperature in the higher temperature range is higher for stocks with sulphenamides. But in the case of stocks with DTB it is seen that at lower temperature increase in rate is higher. This indicates the ability of DTB to accelerate the cure reaction and proves the fact that binary accelerators are capable of vulcanisation at lower temperatures. The effect of DTB with the three sulphenamides is similar in this regard.

The Arrhenius equation was used to calculate the activation energy of the mixes.

$$(t_{90})^{-1} = Ae^{-E/RT} \quad (10)$$

$$-(\log t_{90}) = \log A - E/2.303RT \quad (11)$$

A plot of $-\log t_{90}$ versus $1000/T$ gives a straight line. (Figure 6). The slope of the line is an indication of the fastness of the cure reaction. From the slope of this line, the activation energy (E) can be calculated.

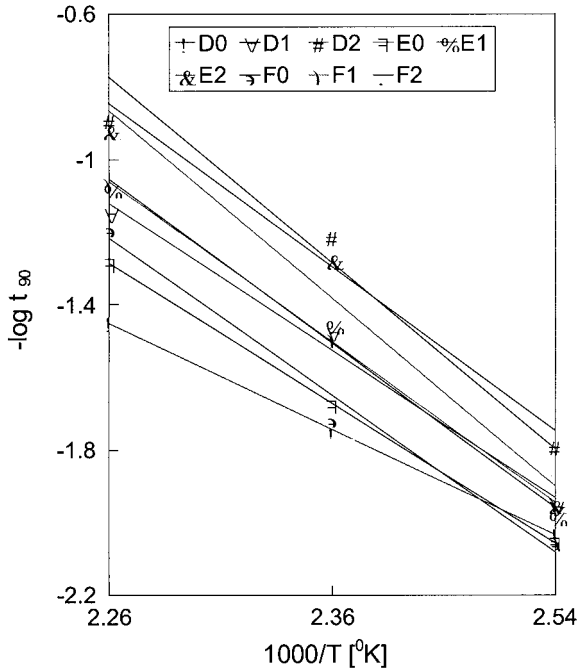


FIGURE 6. Arrhenius plots of mixes showing temperature dependence of cure reactions.

Table 3. Kinetic studies.

	Mix Number								
	D0	D1	D2	E0	E1	E2	F0	F1	F2
Temperature (°C)									
120	0.0086	0.0216	0.0389	0.0083	0.0105	0.0238	0.0056	0.0072	0.0156
150	0.0155	0.0934	0.1499	0.0558	0.0966	0.1255	0.0289	0.0767	0.0965
170	0.0378	0.1462	0.3098	0.1128	0.1857	0.2997	0.1349	0.1978	0.3552
Cure rate index (min ⁻¹)	2.59	4.43	7.5	3.49	5.28	7.03	4.21	5.17	8.6
Energy of activation (kJ/mol)	56.59	38.59	30.65	51.12	40.65	34.2	54.95	45.2	38.6

It is seen that in all cases the slope increases with addition of DTB and maximum slope is shown by compounds with higher amount of DTB. The activation energies of the cure reactions are also given in Table 3. It is seen that the activation energy required for mixes with no DTB is the highest, i.e. this reaction requires much more energy and therefore will start and proceed slowly. The lower the activation energy, the faster will be the cure reaction. It is clear that the activation energy decreases with increasing concentration of DTB, indicating faster initiation of the cure reaction.

Mechanical Properties

The mechanical properties of the vulcanisates are given in Table 4. The stress-strain curves for the vulcanisates are given in Figure 7. With the addition of DTB the strength increases. Maximum strength is shown by vulcanisates with a higher loading of DTB. This may be due to the increase in crosslink density. The modulus values at 300% elongation are also given in Table 4. Hardness and stiffness (modulus) are concepts, which are important to performance in even the least sophisticated applications of rubber. Relationships between curative levels and vulcanisate modulus are therefore fundamental to all rubber compounding. It is found that as the concentration of DTB increases, the modulus values also increase. The mixes with DTB show the maximum modulus.

Tensile strength and the tear strength of the vulcanisates are found to increase with an increase in the concentration of DTB. This could be correlated with the observed crosslink density of the vulcanisates. The tear strength also increases with addition of DTB. The elongation at break values show a decrease as DTB concentration increases. This may

Table 4. Mechanical properties of gum SBR vulcanisates.

	Mix Number								
	D0	D1	D2	E0	E1	E2	F0	F1	F2
Tensile strength (MPa)	3.1	3.98	4.76	3.6	3.8	4.57	3.28	3.89	4.46
Tear strength (N/mm)	6.8	7.5	9.6	7.5	10.6	11.2	8.6	9.2	10.5
Secant modulus [300 %] (MPa)	1.98	2.47	3.65	2.2	2.45	3.24	2.31	2.71	3.32
Elongation at break (%)	559	605	490	620	552	485	540	482	475
Young's modulus (MPa)	0.15	0.39	0.72	0.42	0.477	0.745	0.51	0.55	0.68
Hardness (%)	42	45	46	41	45	43	42	45	45

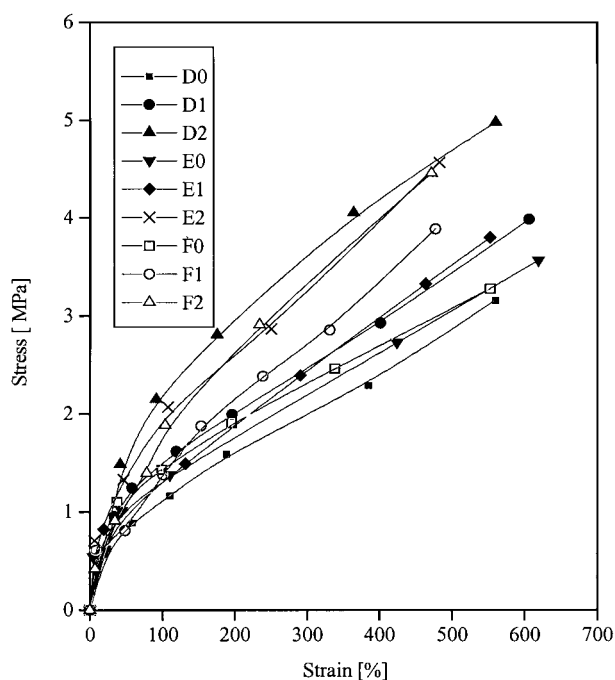


FIGURE 7. Stress-strain curves of SBR vulcanisates.

be due to the decrease in flexibility, resulting from the increase in crosslink density. It may be noted that no optimum concentration is shown by DTB as in our previous studies with natural rubber [12,13]. This may be due to the fact that SBR being less unsaturated requires higher amount of accelerator for appreciable curing. This in turn increases the mechanical properties of the resulting vulcanisates.

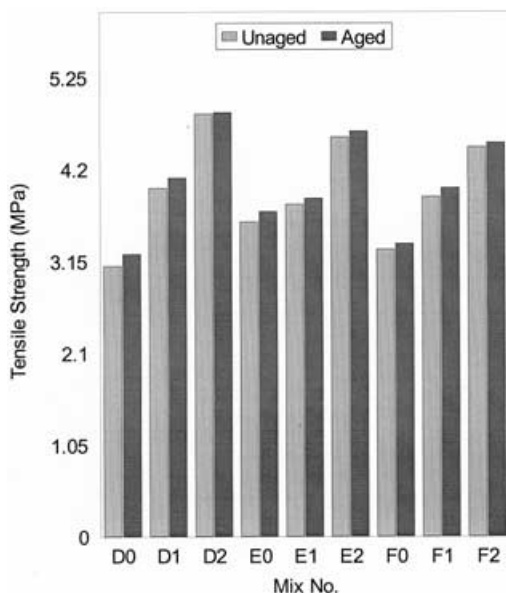


FIGURE 8. Thermal aging resistance of vulcanisates.

The thermal ageing of the samples was carried out at 70°C for 72 h. The tensile strength values register a slight increase after thermal ageing for all the samples. (Figure 8). The slight increase in tensile strength may be due to the formation of additional crosslinking. This is possible since the samples were cured for optimum cure time, which results in formation of only 90% of the total crosslinks. Moreover as the efficient crosslinking system is selected, majority of the crosslinks are mono- and di-sulphidic. These crosslinks are thermally stable. The behavior is similar in samples cured with the primary accelerator alone and the combination of primary and secondary accelerator DTB. This indicates that DTB is not harmfully interacting with sulphenamides in SBR. The resistance of DTB to ageing is clear from these results.

Crosslink Density Measurements

The swelling ratio of the vulcanisates was evaluated in order to find the extent of crosslinking. The calculated values of the crosslink densities are given in Table 5. Swelling and stress-strain measurements were made in order to calculate the crosslink density. The

Table 5. Network characteristics.

	Mix Number									
	D0	D1	D2	E0	E1	E2	F0	F1	F2	
Crosslink density from stress-strain ($\nu \times 10^6$) moles/g	40.23	42.2	57.63	46.7	57.9	83.3	46.7	52.35	60.65	
Crosslink density from swelling ($\nu \times 10^6$) moles/g	18.19	19.8	23.36	16.8	22.4	23.1	21.25	25.49	31.25	
Mono- and di-sulphidic linkages ($\nu \times 10^6$) moles/g	10.24	12.26	14.64	9.88	16.54	17.8	15.64	18.52	20.23	
Polysulphidic linkages ($\nu \times 10^6$) moles/g	7.95	7.57	8.72	5.92	5.96	6.30	5.84	7.97	9.82	
Swelling ratio	7.44	7.24	6.29	7.43	7.38	6.42	6.63	6.20	5.78	

Mooney–Rivlin [14] equation was used for calculating the amount from crosslinks by stress–strain measurements.

$$\nu = \frac{F}{2A_0\rho RT(\alpha - \alpha^{-2})} \quad (12)$$

where ' ν ' is the physically effective crosslink density, F is the force, A_0 is the area of cross section, R is the universal gas constant, T is the absolute temperature and ' α ' is the extension ratio of the sample. In this method, the crosslink density is related to the extension ratio of the samples which are subjected to uniaxial tension.

The relative proportions of crosslinks were estimated by the thiol treatment as explained earlier. The amount of polysulphidic linkages is lower compared to mono- and di-sulphidic linkages. This type of result is expected in efficient crosslinking system. Also it is found that DTB is not influencing this general behaviour.

It can be seen that the crosslink density values follow similar trends in both types of measurements. The highest values are shown by the stress–strain measurements, as expected. This is because the physically effective crosslink density contains a contribution due to the chemical crosslinks, chain entanglements and loose chain ends acting as crosslinks in rubber. The physically effective crosslinks density, is generally higher than the estimated chemical crosslink density because the estimates are based on the concentrations of purely chemical crosslinks without contributions of chain ends and entanglements [15]. The entanglement density calculated from the modulus measurement increases with the addition of DTB and mix with 1.5 phr shows the maximum value. (Table 6). In most of the

cases it is also in accordance with the observed crosslink density value from the swelling and stress-strain measurements.

Dynamic Mechanical Properties

The viscoelastic properties of polymers are markedly dependent on the type of crosslink and the degree of crosslinking. Crosslinking raises the glass transition temperature (T_g) of a polymer by introducing restrictions on the molecular motions of the chain. Low degrees of crosslinking in normal vulcanised rubbers act in a similar way to entanglements, and raise T_g only slightly above that of the crosslinked polymer [16].

The effect of crosslinking is most important and best-understood in elastomers. Sulphur crosslinking of rubbers produces a variety of crosslinking types and crosslink lengths [17]. It is well known that polysulphidic linkages predominate with a conventional sulphur vulcanisation system whereas mono- and di-sulphidic crosslinks are formed with an efficient vulcanisation system, which has a higher accelerator/sulfur ratio. Sulphur also introduces main chain modifications either in the form of pendant groups or as cyclic sulphide linkages that have a large influence on viscoelastic properties. Networks containing high proportions of polysulphidic crosslinks display different mechanical properties from those containing mono-sulphidic or C-C crosslinks. It is shown in the literature that the increase in accelerator level results only in small changes of T_g . Stenberg and co-workers [18] studied the effect of different types of crosslinks on viscoelastic properties of natural rubber. They concluded that the rubbery tensile modulus was dependent on the crosslink density, but almost independent of the crosslink type.

The plots of storage modulus of vulcanisates cured with DTB/DCBS, DTB/TBBS and DTB/MBS as a function of temperature are given in Figures 9–11 respectively. The graphs can be divided into three distinct regions namely, the glassy region, the transition (leathery) region and the rubbery region. A sharp decrease in modulus is observed at the transition from the glassy region to the rubbery region. This point corresponds to the glass transition region. The plateau modulus in the glassy and the rubbery regions are higher for mixes with DTB loading. Mixes with 1.5 phr DTB show the maximum modulus. This could be due to the increased entanglement density due to the addition of DTB.

The loss modulus values are plotted as a function of temperature in Figures 12–14, for the three binary systems DCBS/DTB, TBBS/DTB

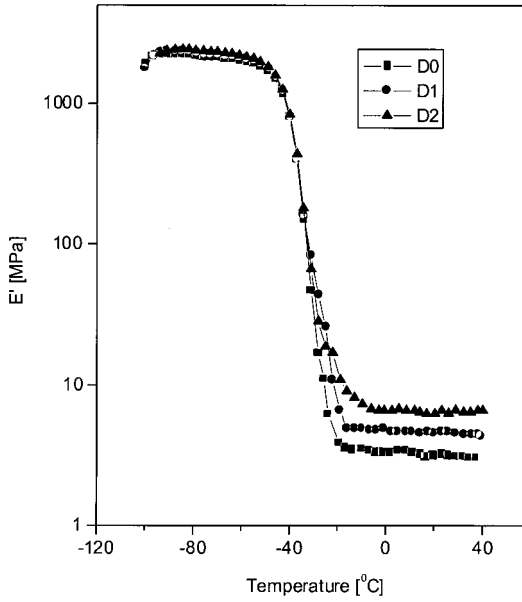


FIGURE 9. Variation of storage modulus with temperature of DTB/DCBS cured vulcanisates.

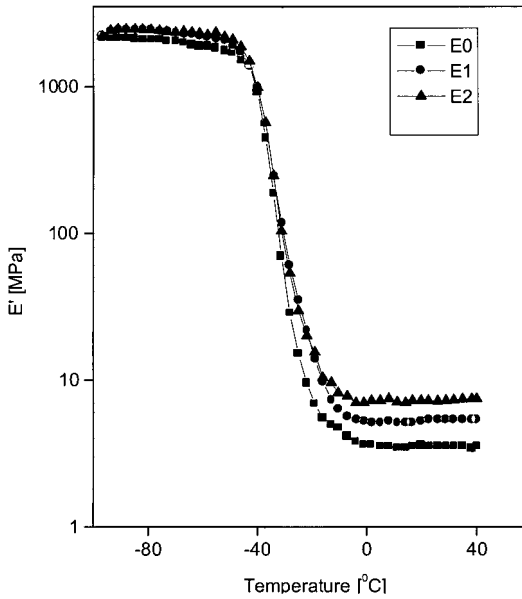


FIGURE 10. Variation of storage modulus with temperature of DTB/TBBS cured vulcanisates.

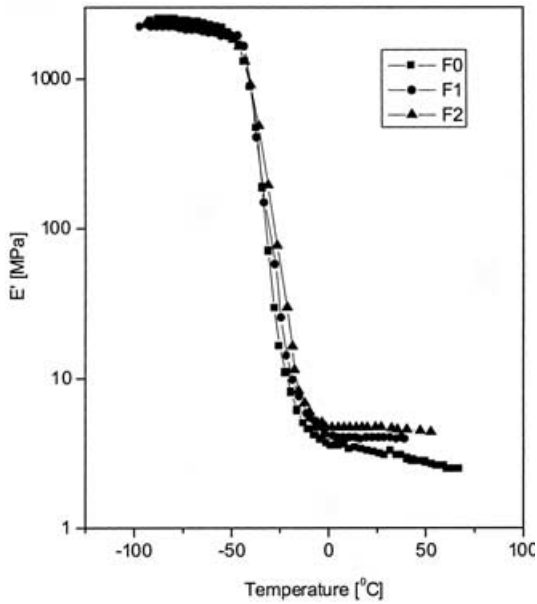


FIGURE 11. Variation of storage modulus with temperature of DTB/MBS cured vulcanisates.

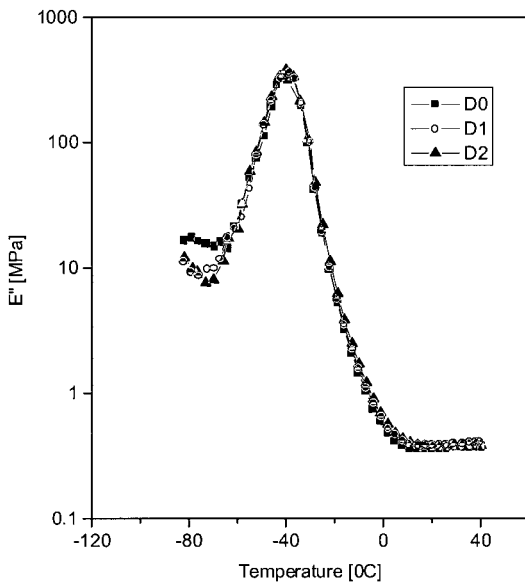


FIGURE 12. Variation of loss modulus with temperature of DTB/DCBS cured vulcanisates.

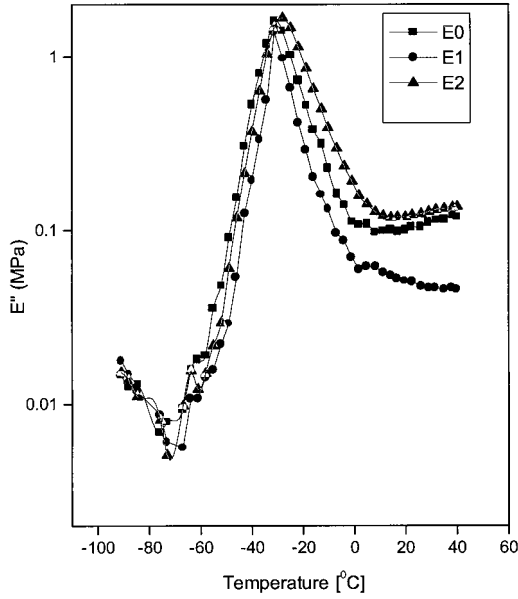


FIGURE 13. Variation of loss modulus with temperature of DTB/TBBS cured vulcanisates.

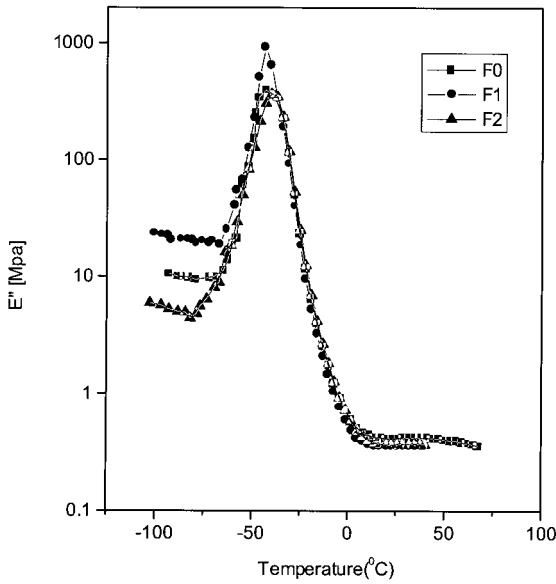


FIGURE 14. Variation of loss modulus with temperature of DTB/MBS cured vulcanisates.

Table 6. Viscoelastic measurements.

		Mix Number								
		D0	D1	D2	E0	E1	E2	F0	F1	F2
Entanglement density $\nu \times 10^4$ (moles/m ³)		2.27	3.133	4.303	2.398	3.338	4.637	2.007	2.639	3.141
Glass transition temperature (°C)	Loss tangent curves	-28.29	-27.84	-27.32	-28.32	-27.1	-27.1	-28.49	-28.45	-28.19
	Loss modulus curves	-40.85	-39.63	-38.47	-43.24	-41.5	-39.47	-43.42	-42.86	-40.34

and MBS/DTB respectively. The peaks of the curves can be taken as the glass transition temperature. As expected the loss moduli (E'') sharply increase in the transition region until they attain a maximum and then decrease with increasing temperature. The T_g values obtained from E'' versus T plots are always lower than those obtained from the $\tan \delta$ maximum. The values are given in Table 6. Similar results are obtained by different researchers [19]. Crosslinking raises the glass transition temperature, T_g of a polymer by introducing restrictions in the molecular motions of the chain. This shifts the glass transition to the positive region. The behaviour observed in all the three binary systems are similar. An increase in crosslink density is indicated with DTB addition with the three primary accelerators.

The plot of $\tan \delta$ as a function of temperature for SBR cured with three binary accelerator systems is given in Figures 15–17. The peak of the curve is taken as the T_g . The T_g values show an increase with increase in crosslink density. The peak width at half height or the peak area is a measure of the damping shown by the compounds. It is directly related to the service performance of the products. The damping shown is similar for the three systems. No significant deviation in damping behaviour is shown by the change in accelerator composition or type. The loss tangent is a sensitive indicator of crosslinking. The T_g values obtained from $\tan \delta$ curves are also given in Table 6. They are found to increase with crosslinking. Crosslink density increases with DTB addition. Similar observations apply to T_g values calculated from loss modulus peaks. At temperatures well above T_g , damping decreases with increasing degree of crosslinking.

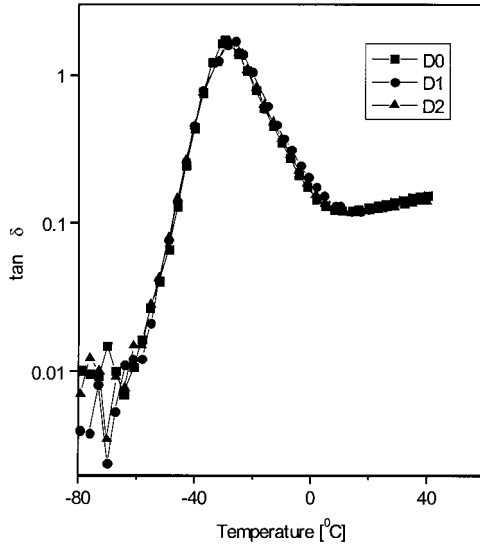


FIGURE 15. Variation of loss tangent with temperature of DTB/DCBS cured vulcanisates.

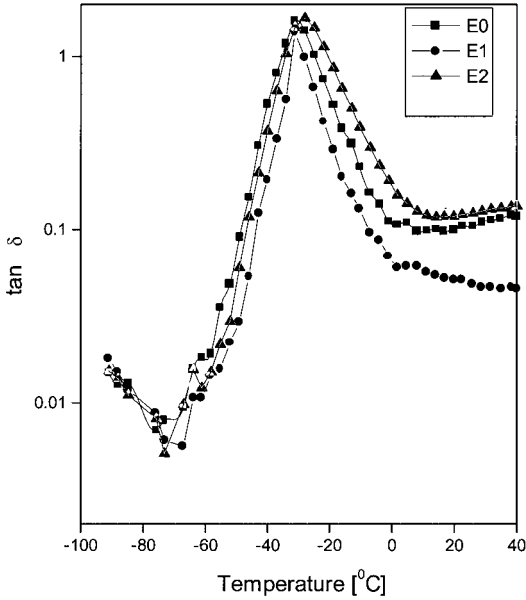


FIGURE 16. Variation of loss tangent with temperature of DTB/TBBS cured vulcanisates.

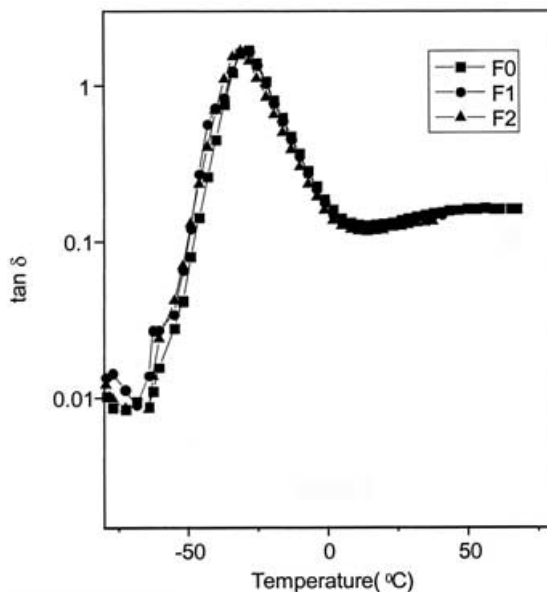


FIGURE 17. Variation of loss tangent with temperature of DTB/MBS cured vulcanisates.

According to the statistical theory of rubber elasticity, the crosslink density for a tetra functional network can be calculated according to the equation

$$\nu = E' / 6dRT \quad (12)$$

where E' is the dynamic storage modulus measured from the rubbery plateau region. Since the storage modulus depends on the frequency used in the measurements the calculated values of entanglement densities are found to increase with increasing DTB loading as shown in Table 6. The mix with 1.5 phr DTB shows the maximum value, which in turn has the maximum entanglement density as shown in Table 5. It is also known that the plateau region modulus increases with increasing accelerator level [20].

Effect of Fillers

The influence of HAF black and silica was studied in DTB cured vulcanisates. Carbon black loading 50 phr was taken for the comparative study. Since the dispersion of silica was found to be difficult, higher loading was eliminated from the present study. The silica loading was

limited to 30 phr. Studies with some sulphur cure system based SBR compounds containing precipitated silica have shown that presence of surface hydration on the filler influences the scorch and cure times of these mixes, i.e longer cure times occur at lower levels of absorbed moisture [21]. Generally carbon black activates the curing process due to the presence of functional groups present on them. The curing behaviour and mechanical properties of the filled vulcanisates was studied in order to get a clear idea about DTB accelerated curing process.

It is seen that optimum cure time increases with silica addition. This is attributed to the absorption of curatives by the functional groups present on silica surface. Cure characteristics of silica and carbon black filled samples are given in Table 7. The mixes selected for this study is having 0.5 phr DTB with the three different primary accelerators. Control compounds without DTB was also done and the results are compared. It is seen that the optimum cure time and scorch time of the mixes decreased slightly with carbon black addition. The cure activation is more in DTB cure samples when compared to the control compounds. This indicates that DTB activates the cure in the presence of carbon black. Silica is found to deactivate the cure as it is observed in control compounds too. But the presence of DTB resists this deactivation to

Table 7. Cure characteristics of silica and carbon black filled mixes.

	Mix Number					
	Carbon black (50 phr)			Silica (30 phr)		
	D1	E1	F1	D1	E1	F1
Maximum torque (dNm)	60.7 (58)	59.4 (57)	58.3 (56.5)	51.9 (49)	53.03 (50.7)	49.3 (46.9)
Minimum torque (dNm)	11.1 (10)	10.5 (10.5)	11.8 (9.5)	10.4 (11)	10.61 (10.5)	10.89 (9.5)
Scorch time (min)	6.1 (25)	5.4 (15.9)	6.2 (20)	16.33 (29)	12.75 (22.4)	13.75 (25.6)
Optimum cure time (min)	24.1 (52.2)	20.25 (45.8)	22.25 (49.2)	37.92 (57.5)	32.75 (48.9)	36.8 (53.2)
Cure rate index (min ⁻¹)	5.55 (3.25)	7.04 (4.2)	6.23 (5.1)	4.63 (3.51)	5 (3.77)	4.33 (3.62)

Values in parenthesis denote control compounds.

Table 8. Mechanical properties of carbon black and silica filled vulcanisates.

	Carbon black (50 phr)			Silica (30 phr)		
	D1	E1	F1	D1	E1	F1
Tensile strength (MPa)	10.62 (9.5)	13.0 (10.2)	13.4 (10)	6.5 (5.2)	5.62 (5.4)	4.86 (4.7)
Tear strength (N/mm)	44.9 (45)	39.6 (40)	42.07 (41)	20.5 (18)	18.4 (16.5)	17.1 (15.2)
Secant modulus [300 %] (MPa)	4.85 (4.5)	4.27 (4.1)	3.94 (3.56)	3.16 (2.98)	2.92 (2.64)	3.65 (3.12)
Elongation at break (%)	1100 (950)	1146 (1050)	1110 (1120)	458 (500)	553 (580)	510 (530)
Hardness (Shore A)	55 (56)	62 (60)	65 (62)	50 (49)	48 (48)	49 (50)

some extent. The cure rate index is increased in carbon black compounds while in silica filled stocks a decrease is seen.

The mechanical properties of the silica filled and carbon black filled vulcanisates are given in Table 8. The tensile strength of SBR vulcanisates increases considerably with carbon black loading. The tear strength also increases to a greater extent. Generally silica filled SBR shows better tear properties. The modulus values are higher for the carbon black filled mixes. Generally an appreciable strength is attained for SBR when it is loaded with reinforcing fillers. The improvement in properties is due to the increase in crosslink density observed with DTB addition. This nature is observed in the case of gum compounds. Hardness also increases with filler loading. The observations made in filler studies are comparable with the control compounds.

CONCLUSIONS

Based on the studies on cure characteristics, physical, mechanical properties and dynamic mechanical properties of SBR vulcanisates it has been found that DTB could be effectively used as a binary accelerator for the sulphur vulcanisation of SBR. The main conclusions that have been made are

- DTB reduces the optimum cure time for SBR vulcanisation.
- DTB can be used with sulphenamides like TBBS, DCBS and MBS to improve cure rate and to impart better processing characteristics.

- Mechanical properties like tensile strength, tear strength and modulus improved with DTB addition. Better resistance to ageing is shown by DTB cured SBR vulcanisates.
- The chemical crosslink density measured by swelling measurements increased with addition of DTB and the values are in good agreement with those calculated by stress–strain measurements.
- Dynamic mechanical measurement reveals increase in entanglement density and enhancement in storage modulus. T_g values are found to increase with DTB addition. No appreciable change is shown in the damping behaviour.
- Silica and carbon black addition in DTB cured SBR results in improved cure characteristics and mechanical properties.

ACKNOWLEDGEMENTS

The financial assistance in the form of Senior Research Fellowship by Council of Scientific and Industrial Research, New Delhi is greatly acknowledged.

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