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Cure Characteristics and Mechanical Properties of Vulcanised Natural Rubber by Using a New Binary Accelerator System

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Natural Rubber was vulcanised with a new binary accelerator system: 1-phenyl-2, 4-dithiobiuret (DTB)/2,4-morpholinothio benzothiazole sulphenamide. The processing characteristics of the mix showed a significant reduction in cure time with the addition of DTB. Mechanical properties of the vulcanisates showed a better performance. DTB does not change the stress-strain nature of natural rubber. The observed mechanical properties could be correlated with network characteristics of the vulcanisates. The chemical characterisation of the vulcanisates was done by swelling measurements. The crosslink density obtained by swelling measurements was compared to that obtained by stress-strain measurements. Based on the processing, mechanical and chemical characterisation of the vulcanisates an optimum concentration of DTB was found.

Key words: cure characteristics; mechanical properties; vulcanised NR; binary, acceleration; 1-phenyl-2; 4-dithiobiuret; 2,4-morpholinothio benzothiazole sulphenamide

Vulcanisation of rubber with sulphur in the presence of sulphur containing accelerators and other additives is of outstanding interest in the rubber industry, especially in the production of automotive tyres and various other rubber products. To obtain better end-use properties, natural rubber (NR) has been subjected to vulcanisation with various types and amount of accelerators.

Accelerators are chemicals used in rubber compounding to reduce the vulcanisation time and to impart better mechanical properties to the end products. Binary accelerator formulations involve the use of two different accelerators in the system, often leading to improved properties. In many cases a synergistic behaviour is observed leading to better properties in the combined system than expected by the rule of mixtures. Previously, studies have been reported regarding the use of binary accelerator[1–5] systems in vulcanisation formulations. Binary accelerators are presently increasingly used in the rubber industry to obtain a best balance in properties. Krejsa and Koenig[6] have explained different ways for characterising and optimising accelerator systems.

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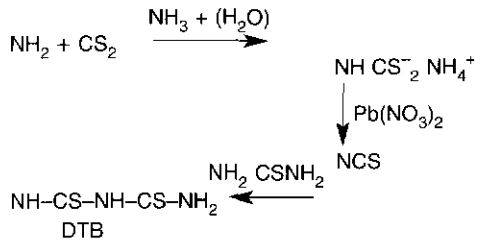
In this paper we have made investigations into vulcanised NR using a new binary system: 1-phenyl-2. 4-dithiobiuret (DTB)/2,4-morpholinothio benzothiazole sulphenamide (MBS). DTB has been synthesized in our laboratory. Studies have been made on the processing, mechanical and network properties of the vulcanisates in order to find an optimum dosage for DTB.



Scheme 1

METHODOLOGY

Materials

Natural rubber used was ISNR-5 obtained from Rubber Research Institute of India. Kottayam. India. The accelerator MBS was obtained from Bayer-AG Germany. Other rubber chemicals. zinc oxide. stearic acid and sulphur were all commercial grades from Ranbaxy, Bombay, India. Propane-2-thiol, 1-hexanethiol and piperidine, analytical grade were supplied by E-Merck, Germany.

1-phenyl – 2, 4 dithiobiuret Synthesis

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 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 recrystallized from ethanol. The sequence of reactions is given in *Scheme 1*.

Compounding and Testing

Compounding of NR was done in the two-roll open mill according to *ASTM-D-16-627*. The stock composition was NR (100 g), zinc oxide (5 p.h.r.), stearic acid (2 p.h.r.) MBS (0.8 p.h.r.) and sulphur (2.5 p.h.r.). The DTB concentration was varied from 0 to 0.8 p.h.r. The rheograph of the mixes and their cure characteristics were obtained using Monsanto Rheometer, R-100. The mixes were cured in hydraulic press at 150°C for the optimum cure time. Tensile properties and tear resistance of the compounds was measured on Instron Tensile testing machine at a cross-head speed of 500 mm/min according to *ASTM-D-412-80* and *ASTM-D-624-81*, respectively.

Hardness of the cured compound was measured according to *ASTM-D-676-52* using a shore A type Durometer. Compression set of the compounds was done according to *ASTM-D-396-61*. The samples, compressed to a particular thickness, were heated in an air oven at 70°C for 22 h. The ageing of the samples was done in an ageing oven at 70°C for 24 h as per *ASTM-D-573*.

Swelling Measurements

A test piece weighing about 0.2 g was cut from the press-moulded rubber sample.

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The sample was immersed in pure toluene in a diffusion bottle for five days at room temperature to reach equilibrium swelling[7]. At the end of this period the test piece was removed, the adhering liquid rapidly removed by blotting with filter paper and the swollen weight immediately measured. The samples were dried in vacuum to constant weight and the desorbed weight was taken. The swelling ratio is defined as:

$$R = (W_1 - W_0)/W_0 \quad \text{... 1}$$

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[8]. The volume fraction of rubber (V_r) in the swollen net work was then calculated by the method reported by Ellis and Welding[9] using the following equation:

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

where D is the de-swollen 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 by the Flory-Rehner equation[10]:

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

where V_s is the molar volume of the solvent and χ the solubility parameter. The value of χ is taken from the literature[11]. Its value is found to be 0.43 for NR-toluene system.

The concentration of polysulphidic crosslinks was estimated from the change in the crosslink density of the vulcanisates before and after treatment with propanethiol and piperidine, which cleave only the polysulphidic crosslinks[12]. Both polysulphidic and disulphidic crosslinks in the vulcanisates could be cleaved by treatment with 1-hexanethiol in piperidine. The determination of crosslink density before and after this treatment gave the concentration of monosulphidic linkages, assuming carbon-carbon linkages to be negligible[13,14].

RESULTS AND DISCUSSION

Curing Characteristics

The rheograph of the rubber mixes is given in *Figure 1*. The only variable in the mixes is the concentration of DTB. It shows that, as the concentration of DTB increased, the time needed for optimum cure (t_{90}) decreased significantly. The processing characteristics are given in *Table 1*. The decrease in cure time is extremely beneficial in increasing the production rate. However the scorch time is decreased. This is in fact affected the scorch safety of the compound. The maximum torque, which is a measure of the stiffness of the compound, increased with increase in concentration of DTB. It is directly related to the modulus of the compound. The cure activating nature of DTB is evident from the processing characteristics of the vulcanisates.

Kinetic Studies

Cure rate index (CRI), which is a measure of the rate of the vulcanisation process, is given by:

$$CRI = 100/(t_{90} - t_2) \quad \text{... 4}$$

TABLE 1. CURE CHARACTERISTICS OF MIXES

Cure characteristics	Mix No.				
	C0	C1	C2	C3	C4
Composition	DTB-0	DTB-0.2	DTB-0.4	DTB-0.6	DTB-0.8
Maximum torque (dNm)	57.31	57.66	58.6	59.6	57.6
Minimum torque (dNm)	6.25	5.77	6.9	5.35	7.76
Scorch time (min)	5.38	3.25	2.08	1.58	1.33
Optimum cure time (min)	12.75	9.33	7.83	7.42	7.79

where t_{90} and t_2 are cure time and scorch time, respectively. *CRI* increased significantly with DTB dosage. This proves the cure activating nature of the secondary accelerator DTB. Studying the kinetics of vulcanisation can make a more standard treatment of this effect by the method reported by Fujimoto *et al.*[15]. 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. The torque values obtained from rheographs are proportional to the modulus of the rubber. Since modulus and torque are analogous, we can substitute torque value for modulus:

$$(a - x) = M_h - M_t \quad ... 6$$

$$a = M_h - M_o \quad ... 7$$

where M_h is the maximum modulus, M_0 is the minimum modulus and M_t is the modulus at time t. When ln $(M_h - M_t)$ is plotted against time t (for Mix C3), a straight line graph was obtained as shown in *Figure 2*. Even though linearity is claimed for the plots, theoretical 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 are obtained for the other combinations. Regardless of temperature and concentration of DTB, all vulcanisation reactions proceed according to first order kinetics. The cure reaction rate constant values, k was obtained from the slope of the respective straight lines. The k values and the cure rate index values are given in *Table 2*. The values increased with temperature.

Arrhenius equation was used in order to calculate the activation energy for cure reaction (E) of the mixes:

$$1/t_{90} = A\, e^{-E/RT} \quad ... 8$$

$$-\log t_{90} = \log A - E/2.303\, RT \quad ... 9$$

A plot of $-\log t_{90}$ *vs.* $1/T$ gives a straight line (*Figure 3*). From the slope of this, E can be calculated. The activation energies of the cure

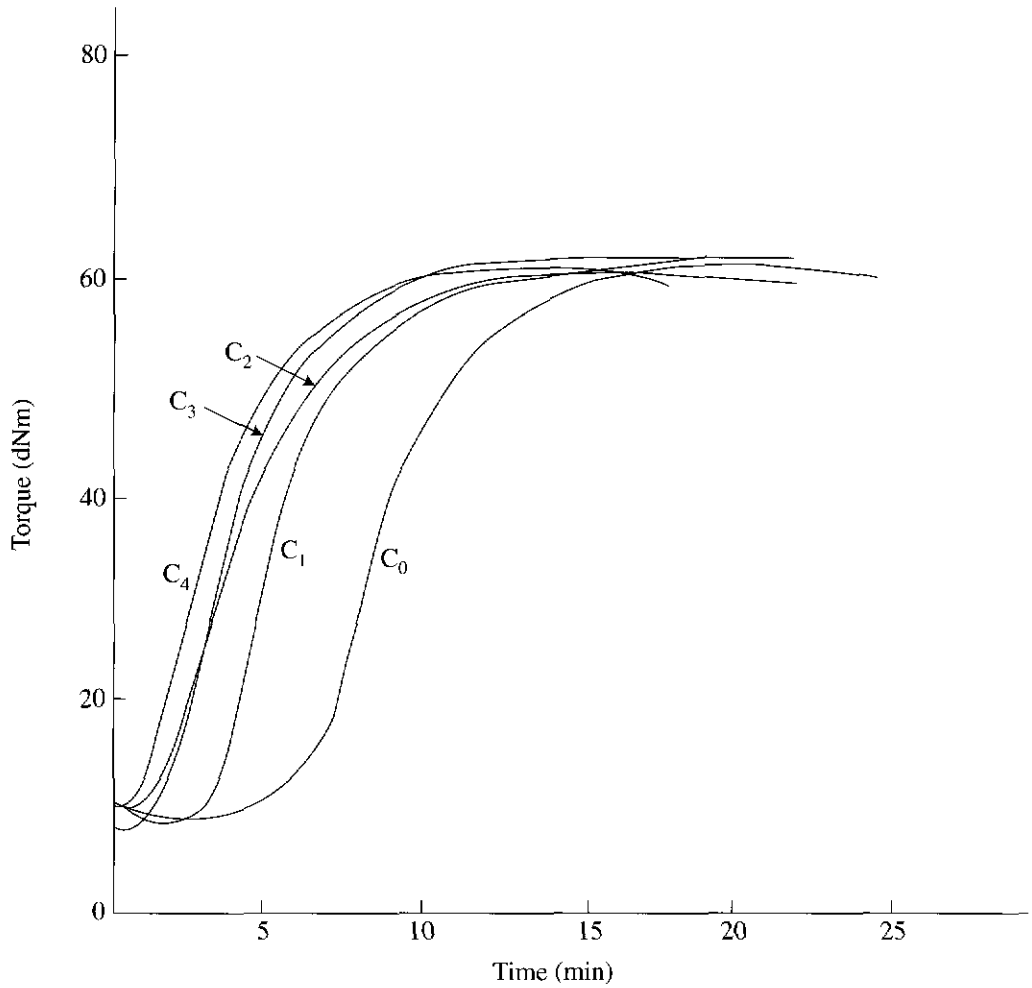

Figure 1. Rheographs of the mixes at 150°C.

reactions are also given in *Table 2*. It shows that the activation energy required for Mix C0 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 indicates that the activation energy decreased with increasing concentration of DTB, indicating faster cure reaction initiation.

Mechanical Properties

The mechanical properties of the vulcanisates are given in *Table 3*. The stress-strain curves for the vulcanisates are given in *Figure 4*. All the curves are of typical elastomeric nature. With the addition of DTB the strength increases. The maximum strength is shown by Mix C3 combination with a concentration of 0.6 p.h.r.

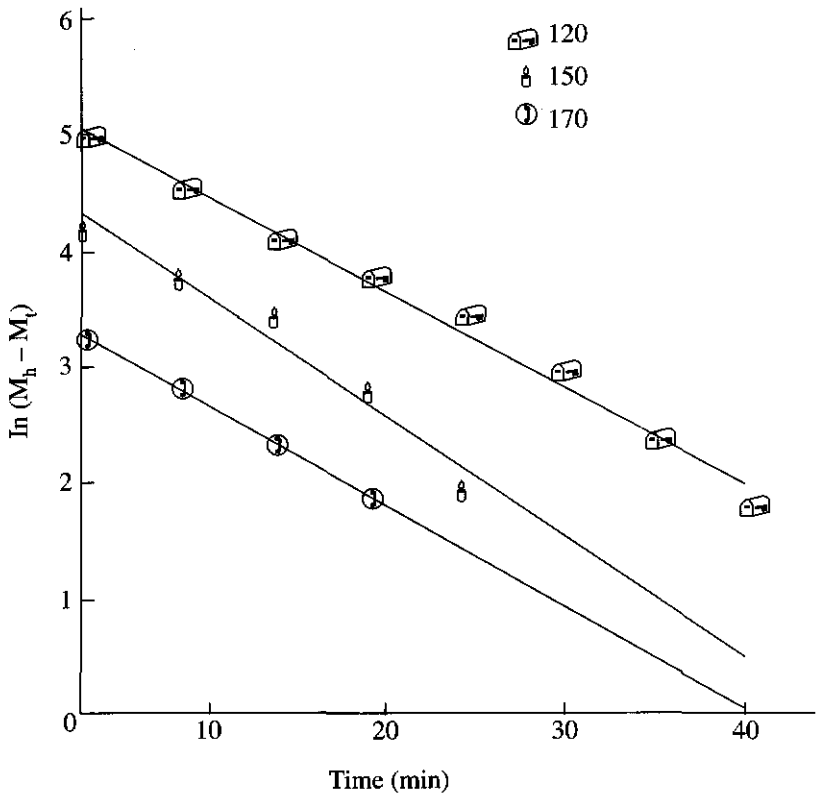

Figure 2. Plots of ln ($M_h - M_t$) against time for the Mix C3.

TABLE 2. CURE KINETICS AND ACTIVATION ENERGY OF MIXES

Temperature (°C)	k-values Mix No.				
	C0	C1	C2	C3	C4
120	0.0231	0.0435	0.0511	0.0520	0.0482
150	0.2958	0.2349	0.3712	0.4113	0.3771
170	0.5519	0.7013	0.5100	0.5195	0.5379
CRI (min^{-1})	13.57	16.45	17.39	17.12	15.48
Energy of activation (kJ/mol)	92	82	81	80	80

TABLE 3. MECHANICAL PROPERTIES OF THE VULCANISATES

Mechanical properties	Mix No.				
	C0	C1	C2	C3	C4
Tensile strength (MPa)	18.9	27.2	29.7	34.5	19.8
Tear strength (N/mm)	29.2	27.4	30.4	35.1	30.5
Elongation at break (%)	1021	929	981	985	889
Modulus at 300% (MPa)	1.35	1.68	1.62	1.77	1.65
Hardness (shore A)	38	38	39	40	40
Compression set (%) at 70%	48	49	47	43	52

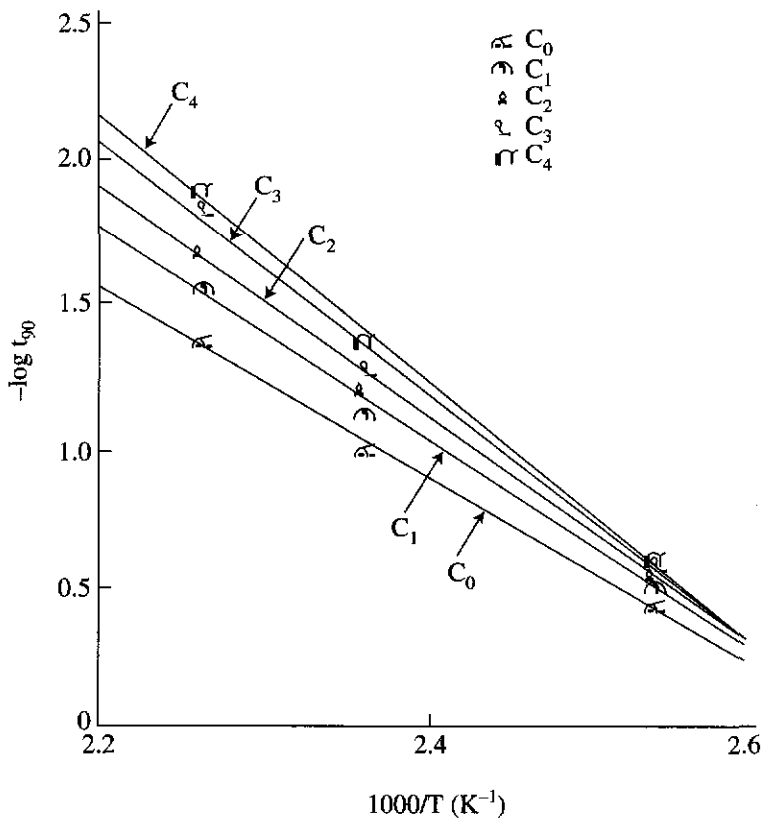

Figure 3. Arrhenius plots of the mixes showing effect of temperature on curing.

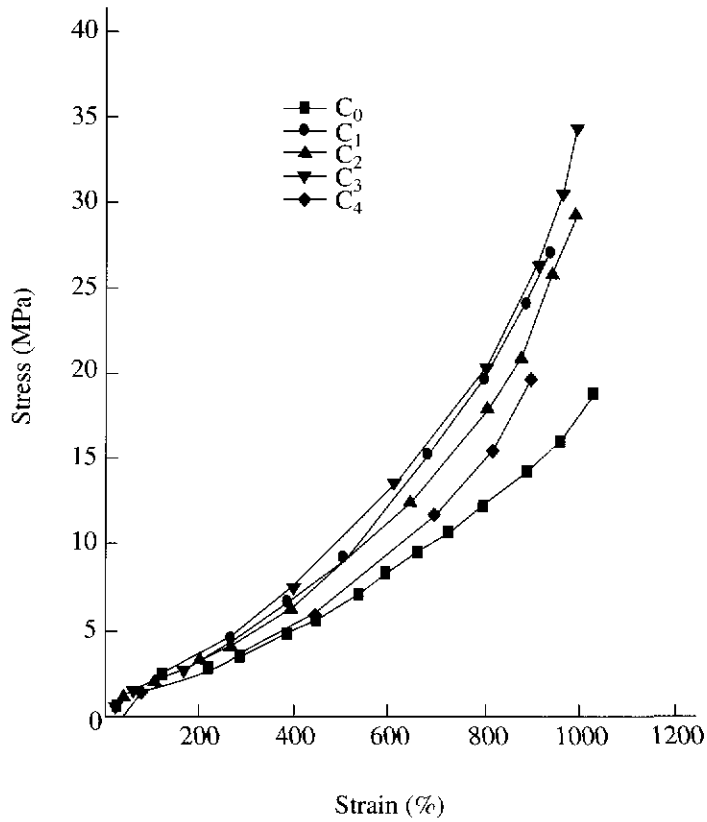

Figure 4. Stress-strain curves of the vulcanisates

DTB. The modulus values at 300% elongation are also given in *Table 3*. It was found that as the concentration of DTB increased the modulus values also increased. The maximum modulus is shown by Mix C3.

The tensile strength of the vulcanisates increased initially and then decreased with DTB concentration. This indicates that, a concentration of 0.6 p.h.r. was optimum for the system. This could be correlated with the observed crosslink density of the vulcanisates, particularly due to the polysulphidic linkages. The tear strength also increased with the addition of DTB. Higher dosages showed the maximum value. The elongation at break values decreased with DTB. A higher elongation indicated a decrease in flexibility with DTB addition. This could be correlated with the observed crosslink density values. Addition of DTB increased polysulphidic linkages. As crosslink density increased, flexibility decreased. This could be the reason for the decrease in elongation.

The compression set and hardness values are also given in *Table 3*. A lower set value is highly advantageous. It is related to both the elastic recovery of the materials and type of crosslinks. Mix C3 showed the lowest value. This can be correlated with the observed crosslink

density values. The increase in crosslink density resulted in better elastic recovery. Hardness increased with DTB addition. Higher dosages of DTB showed maximum values for hardness. The ageing of the samples was done at 70°C for 72 h. In all the cases a decrease in tensile strength values was shown (*Figure 5*). This can be correlated with the predominant polysulphidic linkages formed in the system as shown in *Table 4*. Polysulphidic linkages, which are thermally unstable when, compared to mono and disulphidic linkages will undergo desulphuration or decomposition depending on the concentration of the sulphurating agent. They are more susceptible to temperature. This was evident from the slight reduction in tensile strength values. Even if the amount of polysulphidic linkages was higher in DTB cured vulcanisates, the thermal stability of the vulcanisates was not much affected by ageing. The retention of tensile strength was good in DTB cured vulcanisates. The improved properties shown by Mix C3 may be due to the synergism shown by MBS/DTB binary system.

Crosslink Density Measurements

The calculated values of the crosslink densities are given in *Table 4*. Swelling and stress-strain

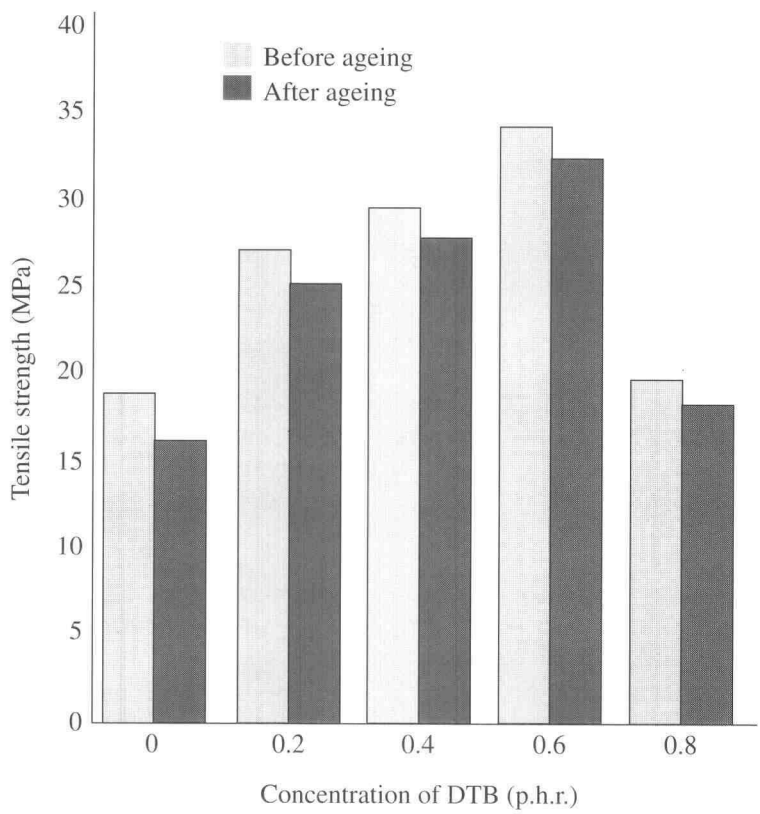

Figure 5. Effect of thermal ageing on tensile strength of the vulcanisates.

TABLE 4. NETWORK CHARACTERISTICS OF THE VULCANISATES.

Mechanical properties	Mix No.				
	C0	C1	C2	C3	C4
Crosslink density from swelling data ($\nu \times 10^5$) gm/cc	3.83	4.10	4.21	4.32	4.16
Polysulphidic linkages ($\nu \times 10^5$) gm/cc	2.11	2.34	2.67	2.99	2.75
Mono and disulphidic linkages ($\nu \times 10^5$) gm/cc	1.72	1.76	1.54	1.33	1.41
Crosslink density from stress-strain data ($\nu \times 10^4$) gm/cc	1.26	1.77	2.11	2.49	1.57
Swelling ratio	3.98	3.83	3.78	3.49	3.79

measurements were done in order to calculate the crosslink density. It is clear from the table that, addition of DTB resulted in the formation of additional crosslinks and this might be the reason for improved mechanical properties. The maximum values are shown by 0.4 p.h.r. and 0.6 p.h.r. DTB. The relative proportion of crosslinks was estimated by the thiol treatment as explained earlier. The amount of polysulphidic linkages was more than that of mono and disulphidic linkages. As the conventional vulcanising system was selected, this result is expected. Swelling ratio was in exact correlation with the crosslink density value of the samples.

Mooney-Rivlin[16] equation was used for calculating the amount of crosslinks by stress-strain measurements:

$$\nu = \frac{F}{2A_0 \rho RT\,(\alpha - \alpha^{-2})} \qquad \ldots 10$$

where ν is the physically effective crosslink density; F is the force at extension ratio α; A_0 is the area of cross section; R is the universal gas constant; and T is the absolute temperature.

It could be seen that the crosslink density values follow a similar trend in both types of measurements. The higher value was shown by the stress-strain measurements, as expected. The physically effective crosslink density was generally higher than the pure chemical crosslink density without contributions of chain ends and entanglements[17]. The physically effective crosslink density contains a contribution due to the chemical crosslinks and another due to the chain entanglements and loose chain ends acting as crosslinks in rubber. Mixes having a DTB concentration of 0.4 p.h.r. and 0.6 p.h.r. showed the maximum value.

CONCLUSIONS

The use of DTB/MBS binary accelerator system in natural rubber vulcanisation using a conventional recipe has been studied based on

the processing, mechanical and network characteristics. It was shown that DTB did not change the strain crystallising nature of NR. The ability of DTB to activate the curing process was clear from the cure characteristics of the vulcanisates. An optimum concentration of DTB was found to be near to 0.4 p.h.r. – 0.6 p.h.r. Higher dosages were found to be inactive. as it had no role in the formation of additional crosslinks. The observed mechanical properties could be correlated with the total chemical crosslink density and the nature of crosslinks. Crosslink density obtained from stress-strain measurements are in good agreement with those obtained from swelling studies. The thermal stability of DTB cured vulcanisates upon ageing was good. Further studies in this area are in progress in order to find the exact mechanism of the DTB accelerated vulcanisation.

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