

Physical, Mechanical, and Viscoelastic Properties of Natural Rubber Vulcanizates Cured with New Binary Accelerator System

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ABSTRACT: Natural rubber was vulcanized with a new binary accelerator system based on 1-phenyl-2,4-dithiobis-urea (DTB) and dicyclohexyl benzothiazyl sulfenamide. A significant reduction in cure time was observed with the addition of DTB. The cure kinetics was investigated and the activation energy was determined. The mechanical properties were improved by adding DTB, and the maximum values are shown at an optimum concentration. Estimates of the concentration of crosslinks and of the relative proportions of different types of crosslinks were made by the chemical characterization of the vulcanizates. The crosslink densities obtained from swelling measurements and stress-strain measurements were compared with those obtained from modulus measurements. All of them follow a similar

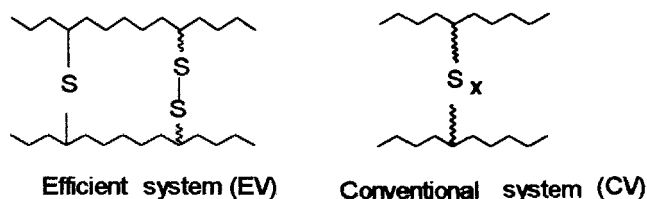
trend and support the observed mechanical properties. A dynamic mechanical analysis of the mixes was carried out and the activation energy was determined from Arrhenius plots. The glass-transition temperature was found to increase with the increase in crosslink density and frequency of measurements. The stress-strain curves were found to not deviate from the strain crystallizing nature of natural rubber. The mechanical properties, network characterization, and processing characteristics were used to optimize the DTB concentration. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2193–2203, 2003

Key words: natural rubber; vulcanization; binary accelerator; dynamic mechanical analysis

INTRODUCTION

Elastomers are one of the oldest and most widely used polymers known, which accounts for their use in a variety of applications. The first significant elastomeric technology advancement was the simultaneous discovery of vulcanization¹ by Goodyear and Hancock. During the vulcanization of rubber compounds and in the course of rubber processing, small quantities of chemicals are used that belong to a group called accelerators. The choice of accelerator in sulfur vulcanization determines the kind of network structure produced and consequently the specific material properties. The chosen accelerator affects the cure rate and scorch safety, as well as the number and average length of the crosslinks formed. The number, distribution, and length of crosslinks all have an influence on the physical properties of rubber. A schematic representation of different types of crosslinks formed by

efficient (EV) and conventional (CV) vulcanization systems is given in the following structure:

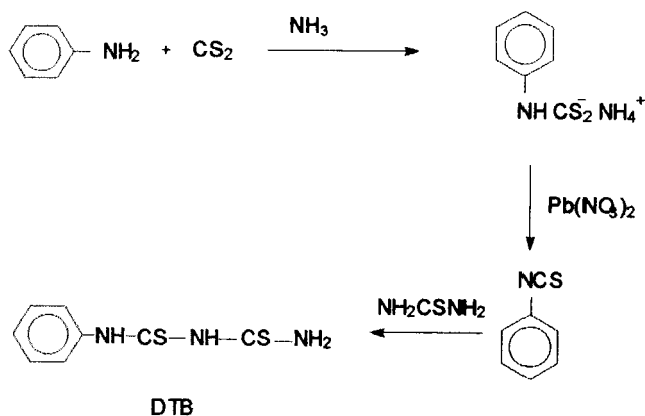


Studies on rubber vulcanization have gained tremendous momentum with the introduction of a new class of compounds called binary accelerators. Because of the reduced time required for curing and production of better end use products, the study of new accelerator systems is still a hot topic of research. Although the mechanism of vulcanization is still open for debate, the use of different curatives has gained importance, depending on their performance. The synergistic behavior of these systems is said to be attributable to the formation of new chemical moieties, which make the curing process easier.

A systematic analysis of the literature indicates that different studies were made on binary accelerator systems via different approaches.^{2–4} One way to illustrate this effect is to measure the mechanical or physical properties as a function of the accelerator ratio and

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Scheme 1 The sequence of reactions in the synthesis of DTB.

correlate the optimum property with the complex formation.⁵ Another method of characterizing binary effects is the extraction of extra network material followed by HPLC analysis of the extract. This approach was followed by Das and coworkers.² Their conclusions are similar to those in Layer's work.⁵ In our laboratory we recently⁶ developed a new binary accelerator system based on 1-phenyl-2,4-dithiobiuret (DTB) and morpholinthio benzothiazole sulfenamide. Investigations were made on the processing and mechanical properties of the vulcanizates cured with the binary system.

The objective of the present study is to evaluate the effect of a new binary system based on DTB and dicyclohexyl benzothiazole sulfenamide (DCBS) in natural rubber (NR). The studies mainly concentrate on the processing, mechanical and dynamic mechanical properties, and network characteristics. The optimum concentration of the accelerator for the best balance of properties was evaluated.

EXPERIMENTAL

Materials

The NR that we used was ISNR-5 obtained from the Rubber Research Institute (Kottayam, Kerala, India). The DCBS accelerator (Vulcavit NZ) was obtained from Bayer-AG. Other rubber chemicals like zinc oxide, stearic acid, and sulfur were all commercial

grades obtained from Ranbaxy Ltd. (Bombay, India). Analytical grade propane-2-thiol, 1-hexanethiol, and piperidine were supplied by E. Merck.

DTB Synthesis

Ammonium phenyl dithiocarbamate was first prepared by the reaction of carbon disulfide with aniline in a strong ammoniacal medium. The product thus obtained was steam distilled with lead nitrate to obtain phenyl isothiocyanate. It was then added dropwise to a stirred solution of thiourea and powdered sodium hydroxide in acetonitrile, and the reaction mixture was heated. When a clear solution resulted, it was diluted with water and acidified with concentrated hydrochloric acid. The crude DTB thus obtained was dissolved in a minimum quantity of aqueous sodium hydroxide to remove any unreacted thiourea. This was then filtered. The alkaline filtrate upon acidification yielded DTB, which was recrystallized from ethanol. The sequence of the reactions is given in Scheme 1.

Compounding and testing

Compounding of NR was carried out on a two-roll open mill according to ASTM D 3182-94. The formulations of the mixes are given in Tables I and II. The rheograph of the mixes and their cure characteristics were obtained using a Monsanto R-100 rheometer. The mixes were cured in a hydraulic press at 150°C for the optimum cure time. The tensile properties and tear resistance of the compounds was measured on an Instron tensile testing machine at a crosshead speed of 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. The 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 Tripsometer according to ASTM D 2632-96. The dynamic mechanical analysis was performed on a

TABLE I
Characteristics of Mixes Cured at 150°C (EV)

Mix no.	A0	A1	A2	A3	A4
Composition (phr)	DTB-0	DTB-0.25	DTB-0.5	DTB-1.0	DTB-1.5
Max. torque (d Nm)	28.82	28.84	30.2	30.8	29.4
Min. torque (d Nm)	6.11	6.45	7.14	7.21	7.48
Scorch time (min)	19.71	4.21	3.0	1.83	1.67
Opt. cure time (min)	26.71	17.88	12.92	7.04	6.0

Stock composition: 100 g NR, 5 phr ZnO, 2 phr stearic acid, 1.5 DCBS, and 0.5 phr sulfur.

TABLE II
Cure Characteristics of Mixes Cured at 150°C (CV)

Mix no.	A5	A6	A7	A8	A9
Composition (phr)	DTB-0	DTB-0.2	DTB-0.4	DTB-0.6	DTB-0.8
Max. torque (d Nm)	48.66	55.05	58.27	59.03	58.41
Min. torque (d Nm)	7.89	7.89	9.13	8.99	8.85
Scorch time (min)	14.92	2.71	1.75	1.25	1.13
Opt. cure time (min)	25.92	12.71	10.75	9.29	8.88

Stock composition: 100 g NR, 5 phr ZnO, 2 phr stearic acid, 0.8 DCBS, and 2.5 phr sulfur.

DMTA MK II machine at a constant strain of 4% and a temperature range of -80 to $+40^\circ\text{C}$.

Swelling measurements

A test piece weighing about 0.2 g was cut from the compression-molded rubber sample. The sample was immersed in pure toluene at room temperature to allow the swelling to reach diffusion equilibrium.⁷ At the end of this period the test piece was taken out, the adhered liquid was rapidly removed by blotting with filter paper, and the swollen weight was measured immediately. The samples were dried in a 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.⁸ The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding⁹ 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 respective densities of the polymer and solvent. The crosslink density was determined using the Flory–Rehner equation¹⁰:

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

where V_s is the molar volume of the solvent and χ is the interaction parameter, which is given by the equation proposed by Hildebrand and Scott¹¹:

$$\chi = \beta + (V_s/RT)(\delta_s - \delta_p)^2 \quad (4)$$

where β is the lattice constant taken as 0.38, R is the universal gas constant, T is the absolute temperature, and δ_s and δ_p are the respective solubility parameters of the solvent and polymer.

The concentration of polysulfidic crosslinks was estimated from the change in the crosslink density of the vulcanizates before and after treatment with propane-2-thiol and piperidine, which cleaves only the polysulfidic crosslinks.¹² Both polysulfidic and disulfidic crosslinks in the vulcanizates could be cleaved by treatment with 1-hexanethiol in piperidine. The determination of the crosslink density before and after this treatment gives the concentration of monosulfidic linkages, assuming carbon–carbon linkages formed during vulcanization to be negligible.^{13,14} Because the samples were difficult to handle after the treatment with 1-hexanethiol, we report the concentrations of mono- and disulfidic linkages together.

RESULTS AND DISCUSSION

Processing characteristics

The rheographs of the EV and CV samples obtained at 150°C are given in Figures 1 and 2, respectively. The only variable in the mixes is the concentration of DTB. The minimum torque in the rheograph can be taken as a measure of the viscosity of the masticated rubber.

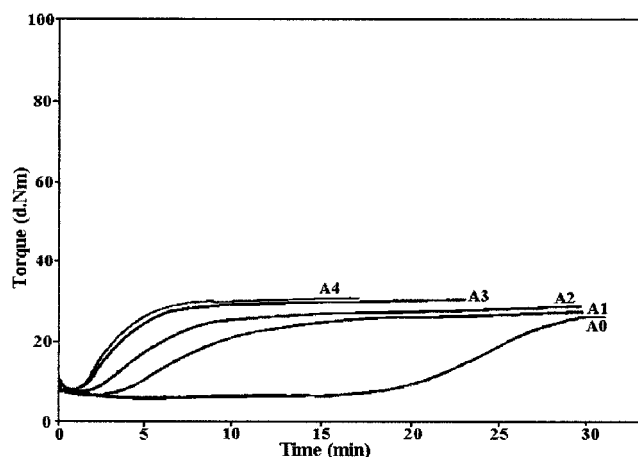


Figure 1 A rheograph of EV mixes.

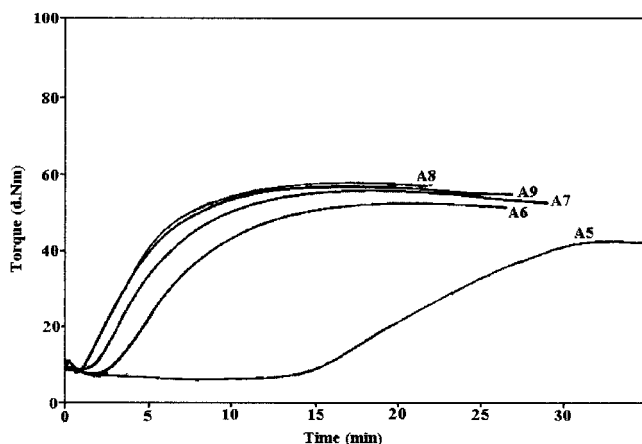


Figure 2 A rheograph of CV mixes.

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 it is roughly a measure of the crosslink density in the sample. As the concentration of DTB increases, the time needed for optimum cure (t_{90}) decreases significantly. The decrease in cure time is extremely beneficial because it increases the production rate. However, the scorch time is found to be decreasing. This in fact affects the scorch safety of the compound. The cure characteristics are given in Tables I and II. The maximum torque, which is a measure of the stiffness of the compound, is found to increase with the DTB concentration. It is directly related to the modulus of the compound. The cure activating nature of DTB is evident from the processing characteristics of the vulcanizates.

Kinetic studies

The cure rate index (CRI) value, which is a measure of the rate of the vulcanization process, increases significantly with the DTB dosage. This further indicates the cure activating nature of the secondary accelerator DTB. A more standard treatment of this effect can be made by studying the kinetics of vulcanization 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, x is the reacted quantity of reactant at time t , and k is the first-order rate constant. For the vulcanization reaction of NR, the rate of crosslink formation is usually monitored by measuring the torque developed during vulcanization. The torque values thus obtained are proportional to the modulus of the rubber. Because mod-

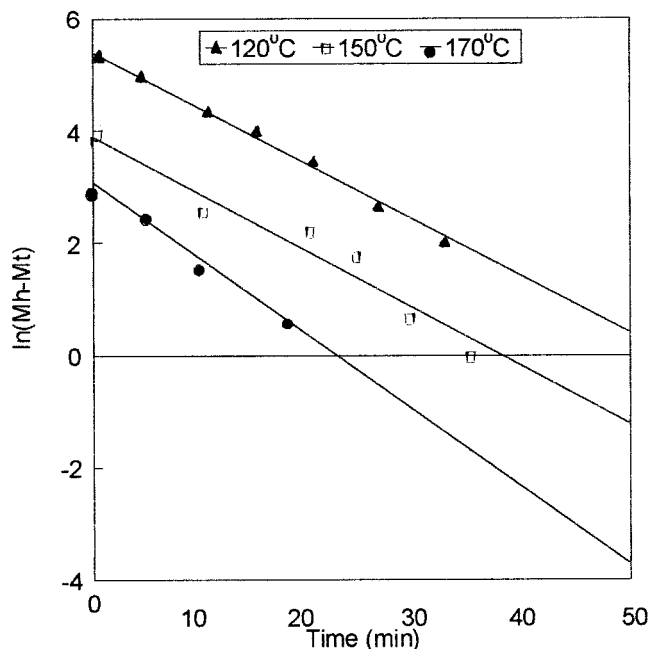


Figure 3 Plots of $\ln(M_h - M_t)$ versus time for mix A3 at different temperatures.

ulus and torque are analogous, we can substitute the torque value for the modulus,

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

$$a = M_h - M_n \quad (7)$$

where M_h , M_n , and M_t are the maximum torque, minimum torque, and torque at time t , respectively. When $\ln(M_h - M_t)$ is plotted against t , a straight line graph is obtained as shown in Figure 3, which proves that the cure reaction of the EV compounds 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 confirms 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 the vulcanization reaction. Regardless of the temperature and concentration of

TABLE III
Cure Kinetics and Energy of Activation of Mixes (EV)

	k values				
	A0	A1	A2	A3	A4
Temperature (°C)					
120	0.0283	0.0448	0.0698	0.0816	0.0849
150	0.0838	0.1839	0.2641	0.3798	0.5229
170	0.3275	0.4454	0.8733	1.6423	1.8424
CRI (s ⁻¹)	6.66	7.32	9.79	19.19	23.09
Energy of activation (kJ/mol)	76	69	65	54	51

TABLE IV
Cure Kinetics and Energy of Activation of Mixes (CV)

	k values				
	A5	A6	A7	A8	A9
Temperature (°C)					
120	0.0245	0.0271	0.0399	0.0619	0.0511
150	0.0964	0.2105	0.2355	0.2752	0.2712
170	0.2897	0.4544	0.7453	0.4784	0.5457
CRI (s ⁻¹)	4.76	10	11.11	12.44	12.90
Energy of activation (kJ/mol)	75	71	68	65	60

DTB, all vulcanization reactions proceed according to first-order kinetics. The cure reaction *k* values are obtained from the slope of the respective straight lines. The *k* values and the CRI values for EV and CV mixes are given in Tables III and IV, respectively. These values increase with temperature.

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

$$(t_{90})^{-1} = Ae^{-E/RT} \tag{8}$$

$$-(\log t_{90}) = \log A - E/2.303RT \tag{9}$$

A plot of $-\log t_{90}$ versus $1000/T$ gives a straight line for the EV (Fig. 4) and CV systems (Fig. 5). The activation energy (E_a) can be calculated from the slope of this line. The activation energies of the cure reactions are also given in Tables III and IV. Note that for the EV system the activation energy required for mix A0 is the highest (i.e., this reaction requires much more energy and therefore will start and proceed slowly).

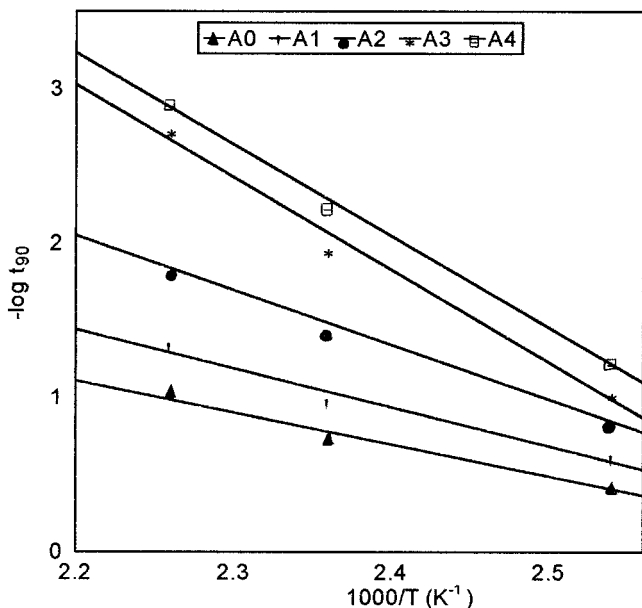


Figure 4 Arrhenius plots for the curing of NR using the DTBS/DTB system (EV).

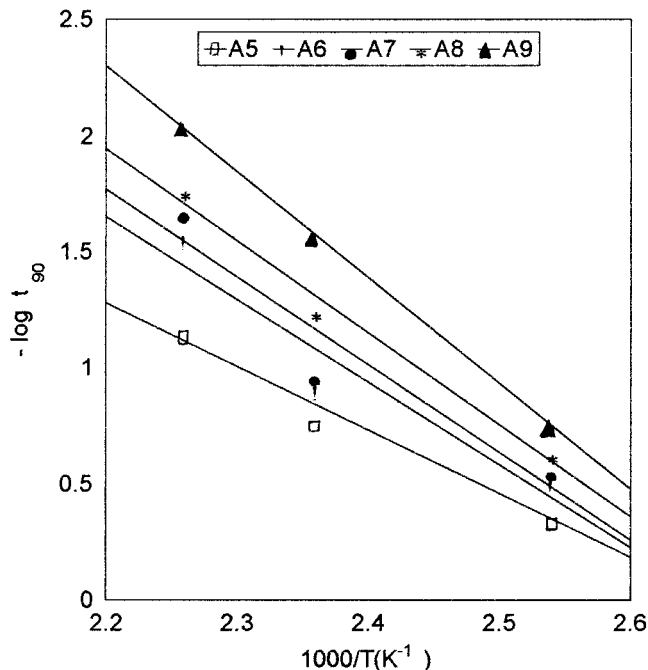


Figure 5 Arrhenius plots for curing NR using DCBS/DTB (CV).

The lower the activation energy, the faster will be the cure reaction. Similarly, in CV systems, the activation energy required is the greatest for A5. 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 vulcanizates are given in Tables V and VI. The stress-strain curves for the vulcanizates are given in Figures 6 and 7 for the EV and CV systems, respectively. All the curves are of a typical elastomeric nature. The strength increases with the addition of DTB. A maximum strength is shown by A3 and A7 combinations at a concentration of 1.0 and 0.4 phr of DTB, respectively. This may be due to the increase in crosslink density. The modulus

TABLE V
Mechanical Properties of NR Vulcanizates Cured Using DCBS/DTB (EV)

	Mix no.				
	A0	A1	A2	A3	A4
Tensile strength (MPa)	8.6	9.5	11.85	15.2	11.25
Tear strength (N/mm)	9.8	10.19	12.36	16.16	13.48
Elongation at break (%)	750	740	723	690	729
Compression set (%)	61	61	56	55	60
Hardness (Shore A)	23	24	23	26	25
Resilience (%)	28	26	24	28	27
Modulus (300%) (MPa)	1.54	1.71	1.91	2.59	2.27

TABLE VI
Mechanical Properties of NR Cured Using DCBS/DTB (CV)

	Mix no.				
	A5	A6	A7	A8	A9
Tensile strength (MPa)	14.22	17.5	29.4	27.7	26.25
Tear strength (N/mm)	18.43	25.89	25.17	26.07	30.47
Elongation at break (%)	930	876	822	850	795
Compression set (%)	78	56	59	78	66
Hardness (Shore A)	31	37	38	40	38
Resilience (%)	23	27	25	26	24
Modulus (300%) (MPa)	3.17	4.06	5.01	4.81	4.71

values at 300% elongation are also given in Tables V and VI. It is found that as the concentration of DTB increases, the modulus values also increase. The maximum modulus is shown by mixes A3 and A7, which have DTB concentrations of 1.0 and 0.4 phr, respectively.

In the case of the EV samples the tensile strength and the tear strength of the vulcanizates are found to increase with an increase in the concentration of DTB. For the CV system the tensile strength first increases and then decreases with the DTB concentration. This result indicates that a concentration of 0.4 phr is the optimum for the CV system. This could be correlated with the observed crosslink density of the vulcanizates. The tear strength also increases with the addition of DTB. The elongation at break values show a decrease in the EV samples as the DTB concentration

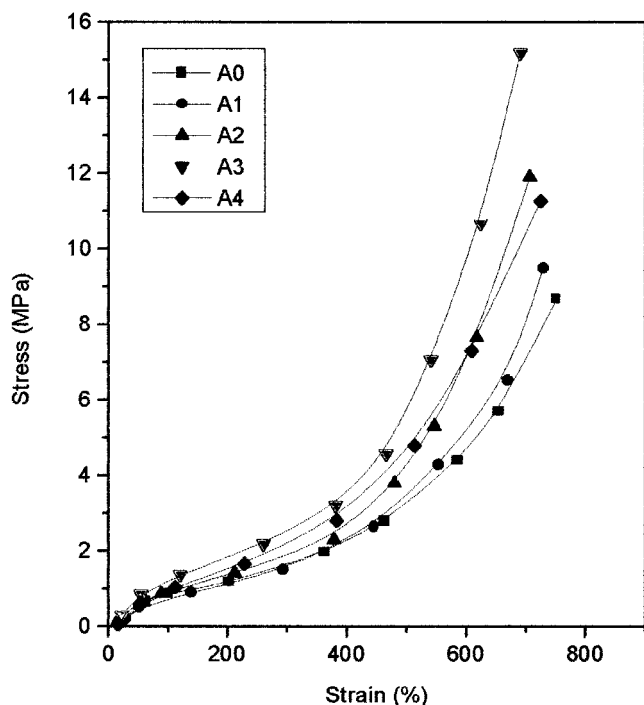


Figure 6 Stress-strain curves for DCBS/DTB cured NR vulcanizates (EV).

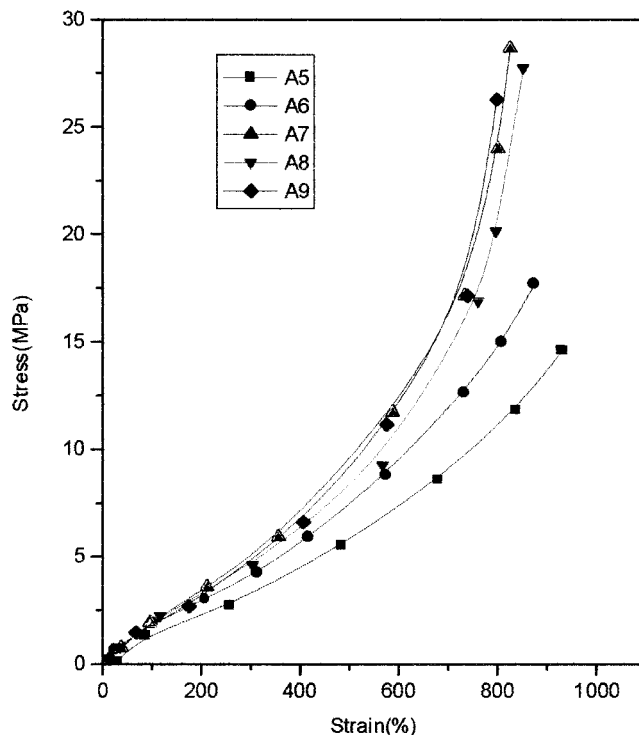


Figure 7 Stress-strain curves for DCBS/DTB cured NR vulcanizates (CV).

increases. This may be attributable to the decrease in flexibility resulting from the increase in crosslink density.

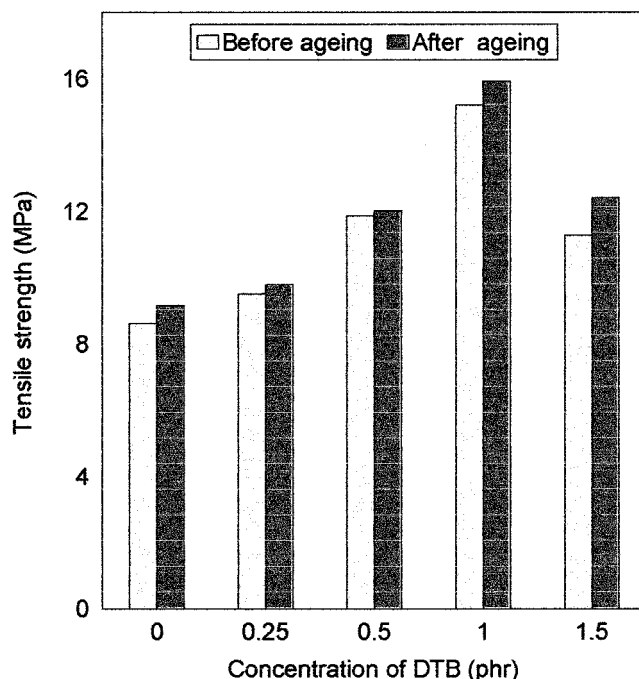


Figure 8 The effect of thermal aging on the tensile strength of EV mixes.

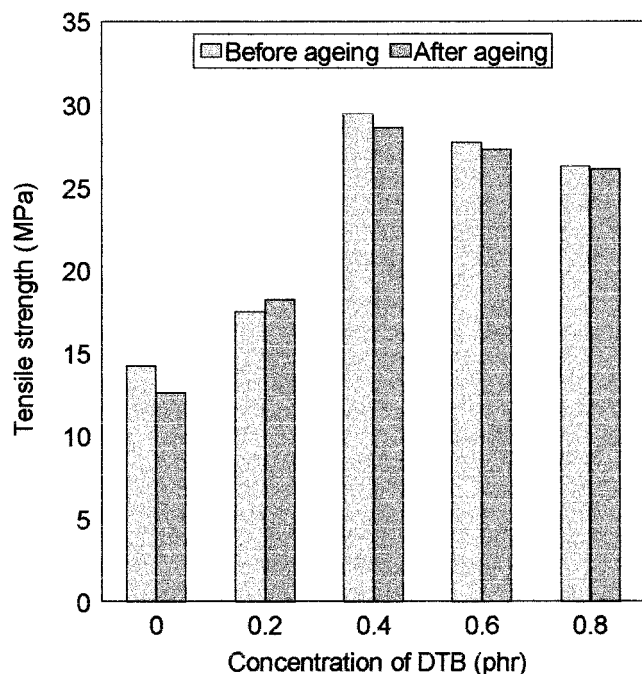


Figure 9 The aging behavior of DCBS/DTB cured NR vulcanizates (CV).

The thermal aging of the samples was carried out at 70°C for 72 h. The tensile strength values register a slight increase for the aged samples in the EV system (Fig. 8). This may be due to the formation of an additional 10% crosslinks for the t_{90} cured samples. As is known, the EV system contains predominantly mono- and disulfidic linkages, which are relatively insensitive to heat. In the CV system a decrease in the tensile strength values is shown (Fig. 9). This can be correlated with the predominance of polysulfidic linkages formed in the system as shown in Table VII. Polysulfidic linkages will undergo desulfuration or decomposition, depending on the concentration of the sulfurating agent. They are more susceptible to temperature. This is evidenced by the reduction in the tensile strength values.

Crosslink density measurements

The calculated values of the crosslink densities are given in Tables VII and VIII. Swelling and stress-strain measurements were made in order to calculate the crosslink density. The Mooney–Rivlin¹⁶ equation was used for calculating the amount from crosslinks by stress–strain measurements.

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

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 that are subjected to uniaxial tension.

The relative proportions of crosslinks were estimated by the thiol treatment as explained earlier. In the EV system, the crosslink density increases with the DTB and the maximum crosslink density is shown by mixes A3 and A4. The amount of polysulfidic linkages is at a minimum in contrast to the mono- and disulfidic linkages, which is supported by previous evidence. In the CV system higher dosages of DTB produce maximum values of the crosslink density. In this case polysulfidic linkages are more prevalent than mono- and disulfidic linkages.

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. The physically effective crosslink density contains a contribution from the chemical crosslinks, chain entanglements, and loose chain ends acting as crosslinks in the rubber. The physically effective crosslink density is in general higher than estimated, because the estimates are based on the concentrations of purely chemical crosslinks without the contributions of chain ends and entanglement.¹⁷ The entanglement density calculated from the

TABLE VII
Network Characteristics of NR Vulcanizates Cured Using DCBS/DTB (CV)

	Mix no.				
	A5	A6	A7	A8	A9
Crosslink density from stress–strain [$\nu \times 10^6$ (mol/g)]	79.7	124.2	203.5	156.5	193.9
Net chemical crosslink density [$\nu \times 10^6$ (mol/g)]	40.78	43.12	48.41	47.46	48.52
Mono- and disulfidic linkages [$\nu \times 10^6$ (mol/g)]	8.53	11.61	10.57	11.10	13.78
Polysulfidic linkages [$\nu \times 10^6$ (mol/g)]	32.25	33.51	37.84	36.36	35.24
Swelling ratio	4.70	4.15	3.85	3.88	3.86

TABLE VIII
Network Characteristics of NR Vulcanizates Cured Using DCBS/DTB (EV)

	Mix no.				
	A0	A1	A2	A3	A4
Crosslink density from stress-strain [$\nu \times 10^6$ (mol/g)]	25.52	37.3	40.37	50.66	59.8
Net chemical crosslink density [$\nu \times 10^6$ (mol/g)]	18.20	20.59	22.10	24.74	24.9
Mono- and disulfidic linkages [$\nu \times 10^6$ (mol/g)]	14.56	15.53	17.53	19.99	20.06
Polysulfidic linkages [$\nu \times 10^6$ (mol/g)]	5.36	9.06	5.57	5.75	5.54
Swelling ratio	8.26	7.38	6.88	6.71	6.62

modulus measurement increases with the addition of DTB, and mix A3 shows the maximum value (Table IX). This is also in accordance with the observed crosslink density value from the swelling and stress-strain measurements.

The optimum concentrations obtained for the new accelerator is explained by the amount and distribution of crosslinks. It is seen from the mechanical behavior and network characteristics that as the concentration of DTB is increased from 1.0 to 1.5 phr in the EV system (Tables V, VIII), a slight decrease in tensile strength is observed, even if the crosslink density shows an increase. This could be due to the desulfuration process taking place. As the accelerator concentration is increased, polysulfidic linkages get converted to mono- and disulfidic linkages. This reduction of polysulfidic linkages results in the decrease in strength. In the CV system (Tables VI, VII), as the concentration of DTB is increased from 0.4 to 0.6 phr, a decrease in strength is observed. In this case also, even if the crosslink density increases, the amount of polysulfidic linkages decreases. This type of behavior is also observed in the modulus.

Viscoelastic properties

The viscoelastic properties of polymers are markedly dependent on the type of crosslinks 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 vulcanized rubbers

act in a similar way to entanglements and raise the T_g only slightly above that of the crosslinked polymer.¹⁸

The effect of crosslinking is the most important and best understood in elastomers. Sulfur crosslinking of NR produces a variety of crosslinking types and crosslink lengths.^{19,20} It is well known that polysulfidic linkages predominate with a conventional sulfur vulcanization system whereas monosulfidic and disulfidic crosslinks are formed with an EV system, which has a higher accelerator/sulfur ratio. Sulfur also introduces main chain modifications either in the form of pendant groups or as cyclic sulfide linkages that have a large influence on the viscoelastic properties. Networks containing high proportions of polysulfidic crosslinks display different mechanical properties from those containing monosulfidic or C—C crosslinks. It is shown in the literature that the increase in the accelerator level only results in small changes of the T_g . Hagen et al.²¹ studied the effect of different types of crosslinks on the viscoelastic properties of NR. They concluded that the rubbery tensile modulus was dependent on the crosslink density but almost independent of the crosslink type.

The plots of the storage modulus as a function of temperature are given in Figure 10. The graphs can be divided into three distinct regions: the glassy region, the transition (leathery) region, and the rubbery region. The plateau moduli in the glassy and rubbery regions are highest for mix A3. This may be because of the increased entanglement density that is due to the addition of DTB.

TABLE IX
Glass-Transition Temperatures (°C)

Mix no.	Frequency (Hz)							
	From tan δ curve				From E'' curve			
	1	10	50	100	1	10	50	100
A0	-40	-36	-32	-32	-46	-42	-37	-37
A3	-35	-34	-28	-29	-41	-37	-34	-32
A4	-37	-35	-31	-31	-43	-40	-38	-36

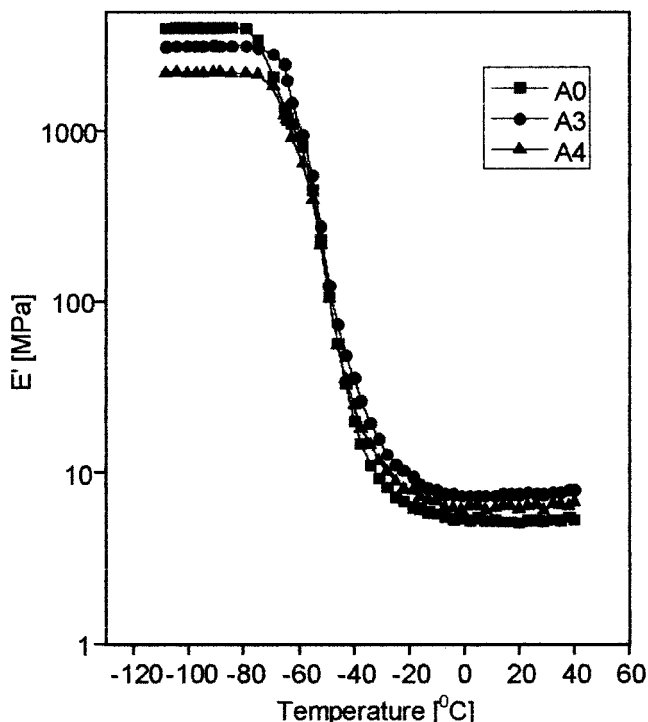


Figure 10 The variation of the storage modulus of DCBS/DTB cured NR vulcanizates with the temperature.

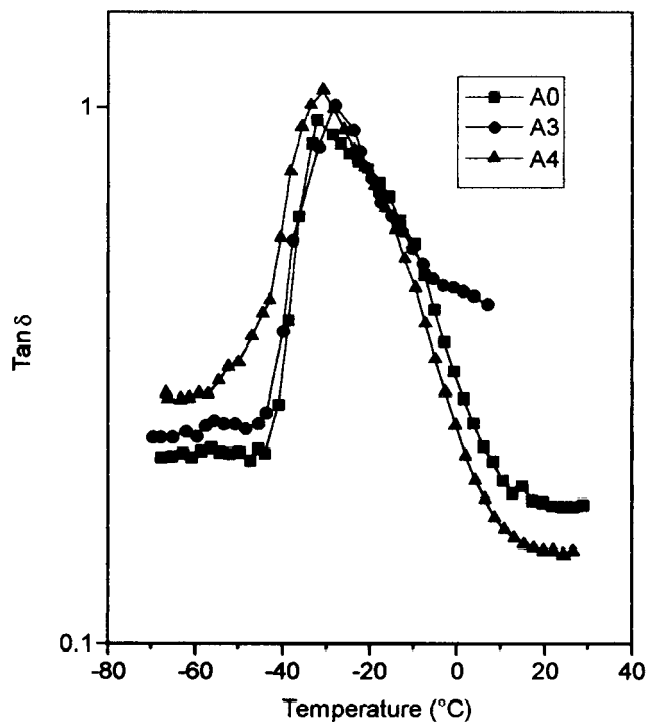


Figure 12 The variation of the loss tangent with the temperature of DCBS/DTB cured NR vulcanizates.

The loss modulus values are plotted as a function of temperature in Figure 11. The peaks of the curves can be taken as the glass-transition temperature. As ex-

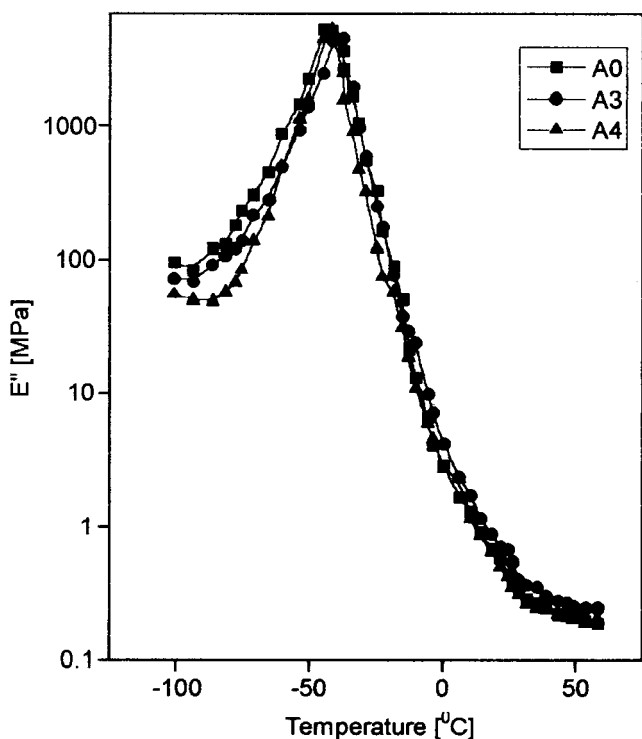


Figure 11 The variation of the loss modulus with the temperature for DCBS/DTB cured NR vulcanizates.

pected, 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 IX. Similar results were obtained by different researchers.²² Crosslinking raises the T_g of a polymer by introducing restrictions in the molecular motions of the chain.

The plot of $\tan \delta$ as a function of temperature is given in Figure 12. The peak of the curve is taken as the T_g . The T_g values show an increase with an increase in the 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.

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

$$\nu = E' / 6RT \tag{11}$$

where E' is the dynamic storage modulus measured from the rubbery plateau region. Because the storage modulus depends on the frequency used in the measurements, the calculated values of the entanglement densities are found to increase with increasing frequency, as shown in Table X.

Measurements performed at high frequencies result in higher modulus values whereas measurements

TABLE X
Entanglement Density [$\nu \times 10^4$ (mol/m³)]

Mix no.	Frequency (Hz)			
	1	10	50	100
A0	3.391	3.51	3.589	3.602
A3	4.458	4.95	4.916	5.121
A4	3.923	4.22	4.522	4.509

made at low frequencies result in lower values. The elastic modulus of a material will decrease over a period of time because of the fact that the material undergoes molecular rearrangement to reduce the localized stresses. The value of E' increases with the frequency at a given temperature. This is due to the lesser mobility of polymeric chains at high frequency. The A3 mix shows the maximum value, which in turn has the maximum entanglement density as shown in Table X. It is also known that the plateau region modulus increases with increasing accelerator level.²¹

The $\tan \delta$ values are plotted against the temperature in Figure 12. The loss tangent is a sensitive indicator of crosslinking. The T_g values obtained from the $\tan \delta$ curves are also given in Table IX. They are found to increase with crosslinking. The crosslink density increases with DTB addition. Mix A3 has the highest crosslink density and the highest T_g . Similar observations apply to T_g values calculated from loss modulus peaks. With an increase in frequency, the T_g increases slightly, as expected. The damping characteristics are similar for all the mixes. At temperatures well above the T_g , damping decreases with an increasing degree of crosslinking.

The activation energy for the glass transition of the samples can be calculated using the Arrhenius equation:

$$f = f_0 \exp(-E/RT) \quad (12)$$

where f is the experimental frequency, f_0 is the frequency as T tends to infinity, and T is the temperature corresponding to the maximum in the $\tan \delta$ curve. The Arrhenius plots are given in Figure 13 and the activation energy values are given in Table XI. The mix having no DTB has the highest activation energy and those containing DTB have lower values.

CONCLUSIONS

The processing, mechanical and dynamic mechanical properties, and chemical structure of NR vulcanizates cured with a new accelerator system have been evaluated in detail. Addition of the new binary accelerator (DTB) was found to increase the rate of vulcanization significantly. The kinetics of the cure reaction was studied in detail and the rate constant values were

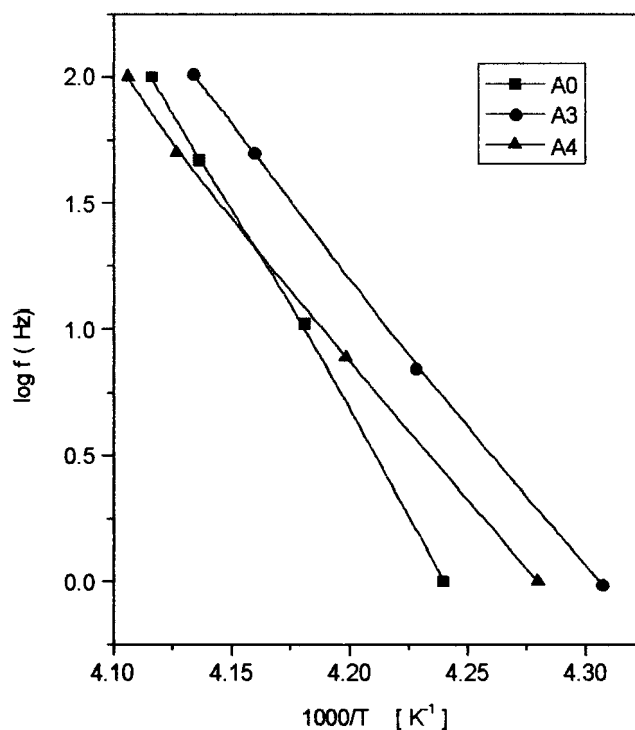


Figure 13 Arrhenius plots for the glass transition of DCBS/DTB cured NR vulcanizates.

compared with CRI values, which were found to be in good agreement. The calculated activation energy indicates the promotion of the cure reaction upon the addition of DTB. It is also seen that DTB increases the torque of the compound during cure, which points toward an increase in modulus. The strain crystallizing nature of NR was found to be unaffected by adding DTB. The mechanical and dynamic mechanical properties of the vulcanizates were found to increase upon the addition of DTB. Increases in the frequency or crosslink density were found to shift the glass-transition temperature positively. The activation energy was found to decrease with the addition of DTB. Crosslink densities from swelling, stress-strain data, and dynamic modulus measurements were compared and found to follow the same trend among the mixes and to account for the observed mechanical properties. Based on the processing, mechanical, and network characteristics, optimum concentrations of 1.0 phr for the EV system and 0.4 phr for the CV system are suggested.

TABLE XI
Activation Energy for Glass Transition

Mix no.	Activation energy (kJ/mol)
A0	67.25
A3	38.69
A4	44.06

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