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Studies on the Cure Characteristics and Vulcanizate Properties of 50/50 NR/BR Blend

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A carbon black filled 50/50 Natural Rubber (NR)/Polybutadiene Rubber (BR) blend is vulcanized using several conventional systems designed by varying the amounts of sulphur and accelerator. The cure characteristics and the vulcanizate properties are compared. The quality and quantity of crosslinks in each case are deciphered by chemical probes to correlate them with the vulcanizate properties.

INTRODUCTION

Blending of elastomers is widely practised to improve the processing characteristics and physico-mechanical properties and to reduce the cost of individual rubbers.¹ Polybutadiene Rubber (BR) has better abrasion resistance than natural rubber (NR), and hence blends of BR and NR are extensively used in the manufacture of tyres.² However, no systematic formulae are available to design a particular compound for an NR/BR blend to achieve a set of vulcanizate properties. Compounds for NR/BR blends are designed based on

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the rule of thumb that BR requires less sulphur and more accelerator than NR.^{3,4} Such a design may not always result in desired properties, especially since NR & BR are not fully compatible.⁵ In this study, a carbon black filled 50/50 NR/SBR blend is vulcanized using several conventional curing systems designed by varying the amounts of sulphur and accelerator and the cure characteristics, network structure and vulcanizate properties are compared.

EXPERIMENTAL

Determination of cure characteristics

The formulations of the mixes employed for the study are given in Table I. The compounds were prepared on a laboratory mixing mill. NR/BR blend was made initially and then the other additives were added in the usual order. The cure curves of the mixes were taken at 150°C on a Monsanto Rheometer model R.100.

TABLE I
Formulations of the mixes

Mix	A	B	C	D	E	F	G	H
Natural Rubber ^a	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Poly Butadiene Rubber ^b	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Phenyl- β -naphthylamine ^c	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HAF Black (N 330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Aromatic oil	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
N-cyclohexyl benzothiazyl ^d sulphenamide (CBS)	0.7	0.7	0.7	0.7	0.6	0.8	1.0	1.2
Sulphur	1.8	2.2	2.6	3.0	2.2	2.2	2.2	2.2

^a $\bar{M}_w = 7.70 \times 10^5$; Mooney viscosity, ML (1 + 4) at 100°C, 85.3; ISNR5 (Rubber Research Institute of India)

^b 97% 1,4 (cis); Mooney viscosity, ML (1 + 4) at 100°C, 48.0

^c Phenyl- β -naphthylamine; Alkali and Chemical Corporation of India Ltd.

^d N-cyclohexyl benzothiazyl sulphenamide; Alkali and Chemical Corporation of India Ltd.

Determination of concentration of chemical crosslinks^{6,7}

The compounds were vulcanized up to the respective optimum cure times on a steam heated laboratory press. Vulcanized sample weighing 0.2–0.3 g was allowed to stand in an excess of toluene containing 0.1% phenyl- β -naphthylamine (PBN) at room temperature (28°C). After equilibrium swelling, the toluene containing PBN was replaced by pure toluene and after two hours swelling was stopped. From the values of the original mass of the test specimen (a_1), of the swollen specimen (a_2) and mass of the specimen after drying for six days at laboratory temperature (a_3) the volume fraction of rubber in the swollen network (V_r) was calculated according to the relation,

$$V_r = \frac{\left(a_3 - a_1 \frac{S_1}{S_2}\right) \frac{1}{\rho}}{\left(a_3 - a_1 \frac{S_1}{S_2}\right) \frac{1}{\rho} + (a_2 - a_3) \frac{1}{\rho_t}}$$

where S_1 = the sum of the contents of zinc oxide and carbon black in the mix (per hundred rubber—phr), S_2 = the sum of the contents of all the components in the mix including rubber (phr), ρ = density of rubber (density of 50/50 NR/BR blend was experimentally found as 0.92 g · cc⁻¹) and ρ_t = density of toluene (0.865 g · cc⁻¹).

The value of V_r so obtained was converted into V_{ro} (the value V_r would have had in the absence of black) by means of the following equation proposed by Kraus

$$V_{ro} = V_r[1 - m\phi/(1 - \phi)]$$

where $m = V_{ro} - 1 + 3c(1 - V_{ro}^{1/3})$, ϕ = Volume fraction of carbon black in the rubber mix and c = parameter for carbon black (in the case of N 330, $c = 1.20$). The degree of crosslinking ($1/2Mc$) was then determined from V_{ro} using the Flory–Rehner equation⁴

$$-\ln(1 - V_{ro}) + V_{ro} + \chi V_{ro}^2 = \frac{\rho V_t V_{ro}^{1/3}}{Mc}$$

where V_t = molar volume of toluene (106.5 cc mol⁻¹) and χ = parameter characteristic of interaction between the rubber network and the swelling agent. For 50/50 NR/BR blend in toluene the

parameter was taken as 0.38.⁸

Determination of concentration of crosslinks after the cleavage of polysulphidic crosslinks.^{6,7}

Test specimen weighing about 0.2–0.3 g (a_1) was allowed to stand in an excess of toluene containing 0.1% PBN for 24 hours at room temperature. Then the solvent was replaced by a solution of 0.4M solution of propane-2-thiol and piperidine in toluene containing 0.5% PBN for 2 hours.

On completion of reaction, the sample was removed from the reagent solution, washed with petroleum ether (bp. 40°C–60°C) four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. The specimen was then kept in an excess of toluene with 0.1% PBN for equilibrium swelling. Finally the vulcanizate was kept in pure toluene for 2 hours and weighed (a_2). The mass of dried test specimen (a_3) was determined after drying for 6 days at laboratory temperature. From the values a_1 , a_2 and a_3 , V_r was calculated as before and the concentration of chemical crosslinks was determined.

Determination of concentration of crosslinks after the cleavage of polysulphidic and disulphidic crosslinks.^{6,7}

Vulcanizate specimen weighing about 0.2–0.3g (a_1) was allowed to stand in 100 ml of 1-hexane thiol in piperidine (1M solution) containing 0.5% PBN for 48 hours at room temperature. The mixture was agitated occasionally. On completion of reaction, the sample was removed from the reagent solution, washed with petroleum ether (b.p. 40°C–60°C) four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. Then the specimen was kept in an excess of toluene with 0.1% PBN for equilibrium swelling. After that the specimen was kept in pure toluene for 2 hours and weighed (a_2). Then it was dried for six days at laboratory temperature and weighed (a_3). The concentration of chemical crosslinks was determined as before.

Determination of amount of free sulphur and sulphide sulphur

Free sulphur was determined iodometrically by converting it to sodium thiosulphate according to ASTM D297-72A. Zinc sulphide

sulphur was determined iodometrically from the formation of cadmium sulphide as described in BS 902, pt 1310-1958.

Determination of mechanical properties

The tensile properties of the vulcanizates were determined according to ASTM D412 (1980) using dumb-bell specimens at 28°C at a crosshead speed of 500 mm per minute using a Zwick Universal Testing Machine. The hardness of the vulcanizates was determined according to ASTM 2240 (1968) and expressed in Shore A units. The ageing resistance of the vulcanizates was determined by keeping the sample at 100°C for 48 hrs in an air oven and then measuring the retention in these properties.

RESULTS AND DISCUSSION

Cure characteristics

Increasing the amount of CBS at constant sulphur level speeds up vulcanization as evidenced by the decrease in cure time and scorch

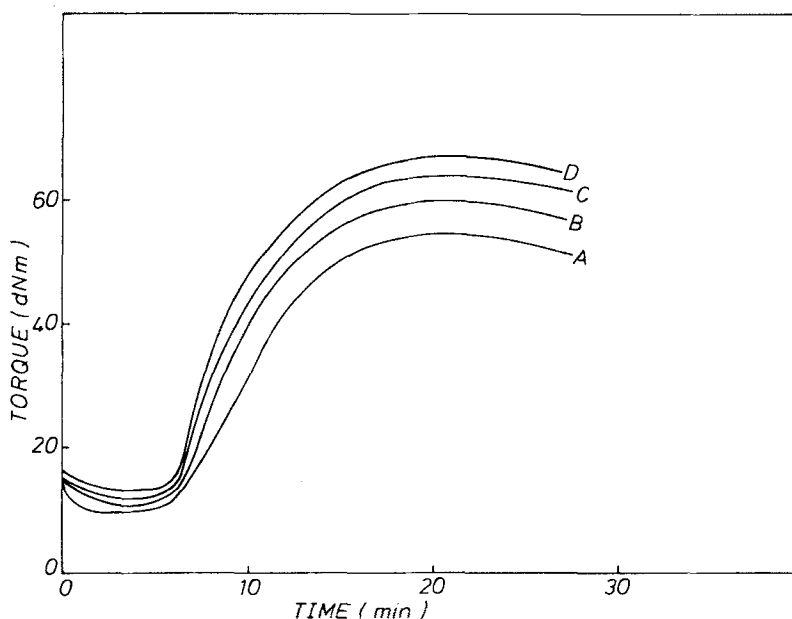


FIGURE 1 Cure curves of the mixes with varying amounts of sulphur.

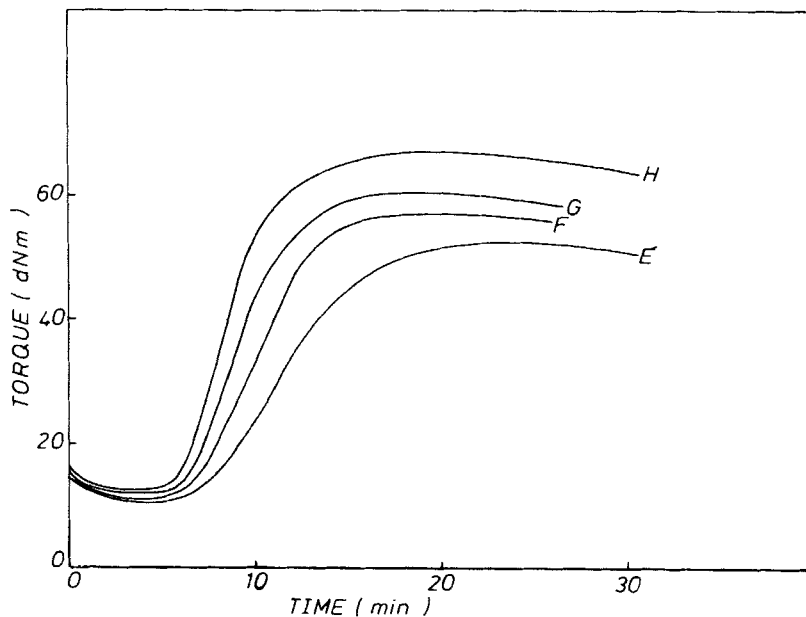


FIGURE 2 Cure curves of the mixes with varying amounts of CBS.

time (Figure 2), as expected. When the amount of sulphur is varied keeping the amount of CBS constant (Figure 1) a definite pattern of change is not visible either in the cure time or in the scorch time. This might be due to lack of complete miscibility of the elastomers. The maximum torque, a measure of the crosslink density, increases steadily with increase in sulphur or CBS. The reverting behaviour of this blend is in striking contrast to that of 50/50 NR/SBR blend.⁹ Whereas, the 50/50 NR/SBR blend is highly resistant to reversion, all the mixes selected for this study show tendency for reversion. This might be due to the formation of a higher percentage of polysulphidic crosslinks in this case than in the case of the NR/SBR blend.

Network structure

Table II shows the results of the chemical characterisation of the vulcanizates. The total crosslink density increases with increase in

TABLE II
Chemical characterization of the vulcanizates

Vulcanizates		A	B	C	D	E	F	G	H
Total crosslink density	$\frac{\text{m.mol}^a}{\text{Kg RH}}$	24.13	28.12	31.42	35.57	23.85	27.42	31.64	35.85
Polysulphidic, disulphidic and monosulphidic crosslinks (%)		b	b	b	b	b	b	b	b
Free sulphur concentration	$\frac{\text{m.mole}}{\text{Kg RH}}$	52.53	57.32	65.62	73.34	58.83	48.82	37.23	29.61
Zinc sulphide sulphur concentration	$\frac{\text{m.mole}}{\text{Kg RH}}$	21.22	28.33	35.82	44.32	31.77	28.33	24.23	20.82
<i>After ageing</i>									
Total crosslink density	$\frac{\text{m.mole}}{\text{Kg RH}}$	19.54	24.67	28.32	34.62	18.63	20.82	23.12	25.52
Polysulphidic crosslinks (%)		51.36	53.12	56.81	59.76	55.32	51.64	48.26	45.79
Disulphidic and monosulphidic crosslinks (%)		b	b	b	b	b	b	b	b
Free sulphur concentration	$\frac{\text{m.mole}}{\text{Kg RH}}$	12.85	15.23	18.42	20.52	12.82	10.32	8.24	6.20

^a $\frac{\text{milli mole}}{\text{Kilogram of rubber hydrocarbon}}$

^b Exact determination is found difficult.

sulphur and/or accelerator. The variation of crosslink density with ageing is interesting. In 50/50 NR/SBR blend, the crosslink density increases with ageing mainly due to the shortening of the polysulphidic crosslinks.⁹ In this blend, which has a higher percentage of polysulphidic crosslinks, the crosslink density decreases with ageing. This might mean that the effect of additional crosslinking induced by the chain shortening effect of the polysulphidic crosslinks is offset by the scission in the main chain. If this is true, this might result in very poor mechanical properties of the vulcanizates after ageing. The difference in crosslink density before and after ageing decreases with increase in sulphur content of the mix. This might be due to an increase in the percentage of polysulphidic crosslinks in the original vulcanizate with increasing sulphur which might have given rise to more crosslinking due to chain shortening. Likewise, the increase in the difference in crosslink density with increase in CBS content might be due to decrease in the percentage of polysulphidic crosslinks in the original vulcanizates with increase in CBS content.

Assuming carbon-carbon crosslinks to be negligible, the proportion of polysulphidic, disulphidic and monosulphidic linkages in the vulcanizates could be estimated by chemical probes. However, the cleavage of polysulphidic linkages in the vulcanizates before ageing led to the breakdown of the vulcanizates, indicating that the majority of the crosslinks are polysulphidic in nature. Likewise, the concentration of monosulphidic linkages in the vulcanizates even after ageing was found to be low since the vulcanizates broke down after the cleavage of polysulphidic and disulphidic linkages. The percentage of polysulphidic crosslinks after ageing increases with increase in sulphur content of the formulation and decreases with increase in CBS content. This might be reflecting the variation of the percentage of polysulphidic linkages in the original vulcanizates. However, the differences between the values might have come down due to the conversion of a fraction polysulphidic linkages into shorter linkages.

The amount of combined sulphur in the vulcanizate may be taken as the amount of sulphur added according to the formulation less the amount of free sulphur and sulphur existing as zinc sulphide. It is observed that the amounts of free sulphur and zinc sulphide sulphur increase with increasing sulphur but decrease with increasing accelerator in the mix. The amount of ZnS sulphur remains more or less constant with ageing, but part of free sulphur seems to get used up in further crosslinking during ageing.

Mechanical properties

The tensile strength of the vulcanizates improves with increase in sulphur content or CBS content whereas elongation at break decreases (Figures 3 and 4). This is obviously due to the increase in crosslink density induced by additional amounts of sulphur and/or accelerator. The increase in tensile strength with increase in sulphur content is more than with CBS content, which might be due to the larger percentage of polysulphidic crosslinks in the former case. Both tensile strength and elongation at break are severely deteriorated with ageing which might be due to the extensive main chain scission. The retention in these properties seems to decrease with increase in sulphur content in the mix. The progressive decay in tensile strength might be due to a higher amount of polysulphidic

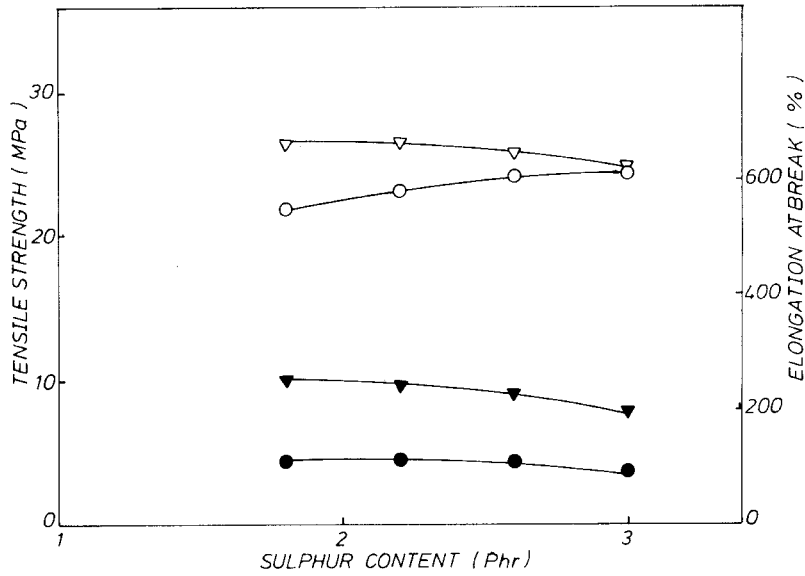


FIGURE 3 Variation of tensile strength and elongation at break with sulphur content: ○,△ before ageing; ●,▲ after ageing.

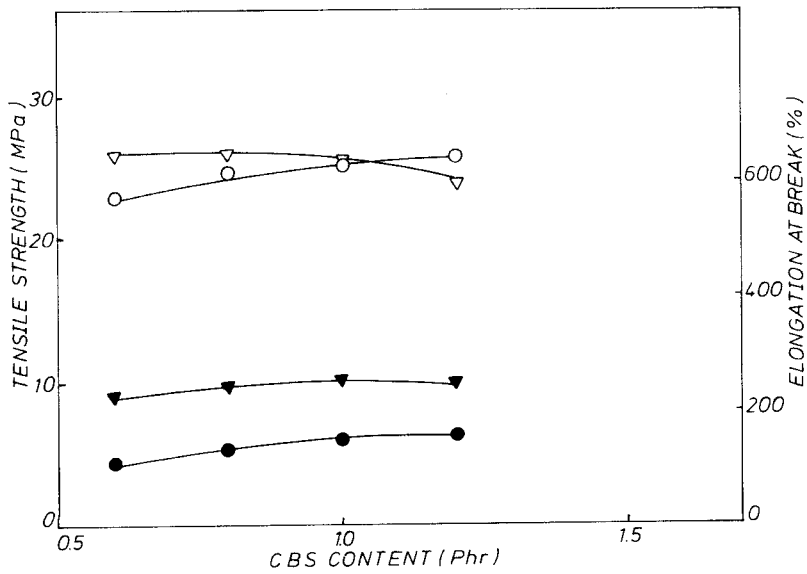


FIGURE 4 Variation of tensile strength and elongation at break with CBS content: ○,△ before ageing; ●,▲ after ageing.

linkage getting shortened, while that of elongation at break, due to the increase in crosslink density because of the same reason. The retention in these properties is found to improve with increase in CBS content which could also be explained on similar lines.

Hardness and modulus, which are direct measures of the crosslink density, improve with increase in sulphur and/or accelerator (Figures 5 and 6). Whereas these properties improve with ageing for 50/50 NR/SBR blend, these decrease in the case of 50/50 NR/BR blend. This is obviously due to decrease in crosslink density with ageing. The retention in these properties improves with increase in sulphur content since the decrease in crosslink density is the least when sulphur content is maximum. Likewise the retention of these properties decreases with increase in CBS content. The mechanical properties of the blends are found to be highly dependent upon the blending parameters. This might be due to phase inversion phenomenon observed in 50/50 NR/BR blends.⁵

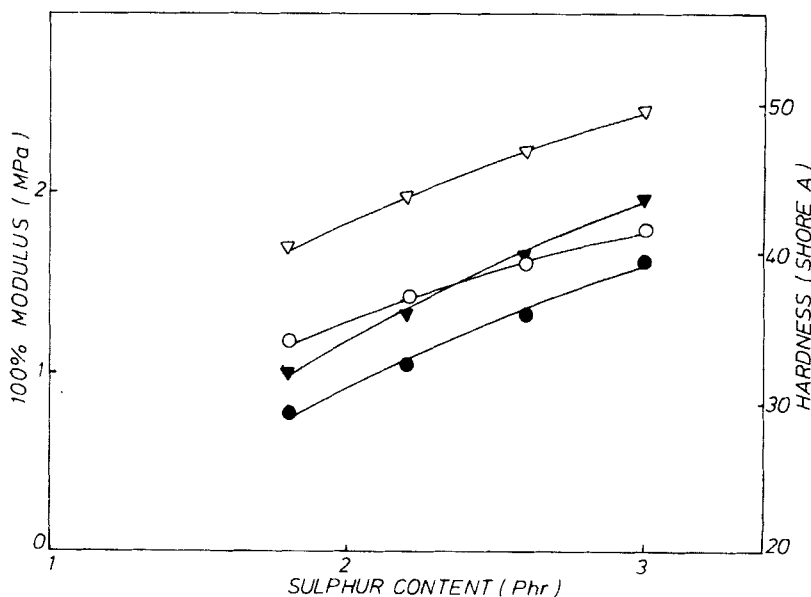


FIGURE 5 Variation of 100% modulus and hardness with sulphur content: ○, △ before ageing; ●, ▲ after ageing.

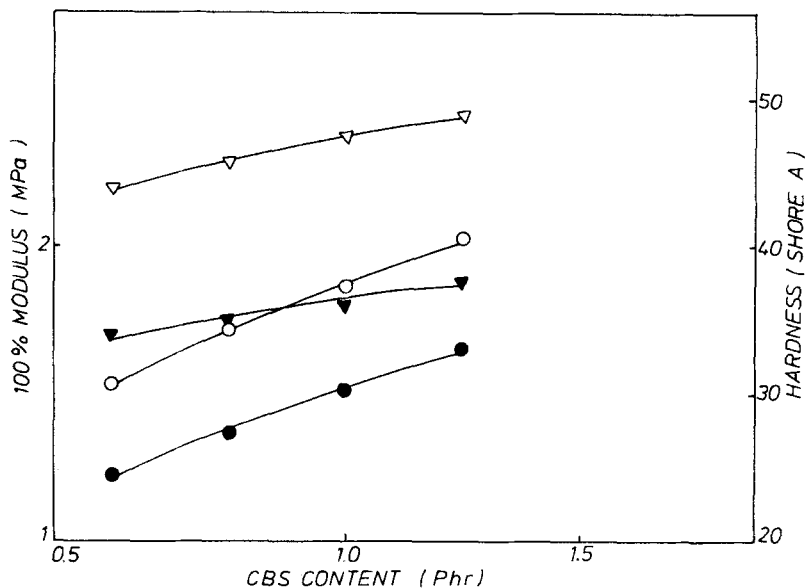


FIGURE 6 Variation of 100% modulus and hardness with CBS content: ○, △ before ageing; ●, ▲ after ageing.

CONCLUSIONS

The following conclusions could be drawn about the cure characteristics, network structure and vulcanizate properties of 50/50 NR/BR blend.

- i) conventional curing systems produce a large proportion of polysulphidic crosslinks. This produces a reverting cure in most cases.
- ii) Extensive main chain scission occurs during ageing which accounts for the reduction in the overall crosslink density with ageing. This results in severe deterioration in mechanical properties.
- iii) The blending parameters have an important say in the vulcanizate properties.

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