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Studies on 50/50 Natural Rubber/Styrene Butadiene Copolymer Blend

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Dedicated to Prof. R. Anantaraman on his 61st birthday

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SUMMARY:

A carbon black filled 50/50 natural rubber (NR)/styrene-butadiene rubber (SBR) blend is vulcanized using several conventional curing systems designed by varying the amounts of sulphur and accelerator. The cure characteristics and the properties of the vulcanizates are compared. The quantity and quality of crosslinks in each case are evaluated by chemical probes to correlate them with the vulcanizate properties.

ZUSAMMENFASSUNG:

Ein mit Ruß gefülltes 50/50 NR/SBR-Blend (Naturkautschuk/Styrol-Butadien-Copolymer) wurde unter Verwendung verschiedener konventioneller Vernetzungssysteme, die durch unterschiedliche Schwefel- und Beschleunigeranteile gekennzeichnet sind, vulkanisiert. Die Vulkanisationscharakteristiken und die Eigenschaften der Vulkanisate wurden verglichen. Das Ausmaß und die Qualität der Vernetzungsstellen wurden für jeden Fall durch chemische Testmethoden ermittelt, um sie mit den Vulkanisateigenschaften zu vergleichen.

1. Introduction

The technology of polymer blends has developed to an important segment of polymer science in the past decade. It is the ability of polymer blends to better satisfy end-use requirements than the existing single polymers that has contributed mostly to this development. It is also more economical to blend polymers for meeting application requirements than to design new materials and construct new facilities to produce them.

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The largest use of polymer blends is in the tire market. Nearly every component in a tire is comprised of a blend of elastomers. Blends of natural rubber (NR) and styrene-butadiene rubber (SBR) are extensively utilized in tire markets, particularly in truck tire applications¹. SBR is slightly less resilient than NR but has better abrasion resistance and weatherability². No definite rules are available for designing a compound of a NR/SBR blend for achieving a set of vulcanizate properties. The compounds are now designed based on the rule of thumb that SBR requires less sulphur and more accelerator than NR because of the lower unsaturation of SBR³⁻⁵. In this study, a carbon black filled 50/50 NR/SBR blend was cured using several conventional curing systems, designed by varying the amounts of sulphur and accelerator, and the cure characteristics are compared. The mechanical properties of the vulcanizates before and after ageing are also compared.

The single most important factor in determining physical properties of rubber vulcanizates is, of course, the degree of crosslinking. Sulphur vulcanizing systems form mono-, di-, and polysulphidic species, the proportions of which also affect the physical properties. During service, the degree of crosslinking may increase or decrease depending upon the elastomer, the temperature and other factors with a possible rearrangement in the nature of crosslinks⁶. The degree of crosslinking of the vulcanizates along with proportions of mono-, di-, and polysulphidic linkages is also estimated before and after ageing to correlate it with the mechanical properties.

2. Experimental

2.1 Determination of Cure Characteristics

The formulations of the mixes and their cure characteristics are given in Tab. 1. The compounds were prepared on a laboratory mixing mill. NR/SBR blend was made initially and then the other additives were added in the usual order. The cure characteristics of the mixes were determined at 150°C on a Monsanto Rheometer model R-100.

2.2 Determination of Concentration of Chemical Crosslinks^{7,8}

The vulcanizate sample weighing 0.2–0.3 g was allowed to stand in an excess of benzene containing 0.1% N-phenyl-β-naphthylamine (PBN) at room temperature (28°C). After 24 h the benzene containing PBN was replaced by pure benzene and after 2 h swelling was stopped. From the values of the original mass of the test

Tab. 1. Formulations and cure characteristics of the mixes.

Mix	A	B	C	D	E	F	G	H
Formulations								
NR ^a	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
SBR ^b	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
ZnO	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
PBN ^c	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HAF black (N330) ^d	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
CBS ^e	0.8	0.8	0.8	0.8	0.6	1.0	1.2	1.4
Sulphur	1.8	2.0	2.5	3.0	2.0	2.0	2.0	2.0
Cure characteristics								
Scorch time, min	6.5	6.5	6.0	6.0	6.0	6.0	6.0	6.0
Optimum cure Time, min	17.5	17.0	16.5	16.0	20.0	15.0	13.0	12.0
Maximum torque, dNm	74.0	82.0	92.0	100.0	72.0	84.0	90.0	94.0
Reversion, number of units dropped in 5 min	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

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

^b 23.5% styrene; Mooney viscosity, ML (1 + 4) at 100°C, 49.2.

^c N-phenyl-β-naphthylamine; Alkali and Chemical Corporation of India, Ltd.

^d High abrasion furnace.

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

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specimen (a_1), of the swollen specimen (a_2), and mass of the specimen after drying for six days at room temperature (a_3) the volume fraction of rubber in the swollen network (V_r) was calculated according to the relation⁹

$$V_r = \frac{(a_3 - a_1 S_1/S_2) \frac{1}{\rho}}{(a_3 - a_1 S_1/S_2) \frac{1}{\rho} + (a_2 - a_3) \frac{1}{\rho_b}}$$

where S_1 = sum of the contents of zinc oxide and carbon black in the mix (per hundred rubber — phr)

S_2 = sum of the contents of all components in the mix including rubber (phr)

ρ = density of rubber (the density of the 50/50 NR/SBR blend was experimentally found as 0.93 g/cm³)

and ρ_b = density of benzene (0.875 g/cm³)

The value of V_r so obtained was converted into V_{r0} (the value V_r would have had in the absence of black) by means of the Kraus' equation¹⁰.

$$V_{r0} = V_r [1 - m\phi/(1 - \phi)]$$

where $m = V_{r0} - 1 + 3c [1 - (V_{r0})^{1/3}]$

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 $\left(\frac{1}{2Mc}\right)$ was then determined from V_{r0} using the Flory Rehner equation¹¹

$$-\ln(1 - V_{r0}) + V_{r0} + \chi V_{r0}^2 = \rho \frac{V_b (V_{r0})^{1/3}}{Mc}$$

where V_b = molar volume of benzene (90 cm³/mol)

and χ = parameter characteristic of interaction between the rubber network and the swelling agent. For 50/50 NR/SBR blend in benzene, the parameter was taken as 0.38.

2.3 Determination of Concentration of Crosslinks after the Cleavage of Polysulphidic Crosslinks^{7,8}

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

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reagent solution, washed with petroleum ether (bp. 40 °C – 60 °C) four times, surface dried on filter paper as quickly as possible, and dried i. vac. to constant weight at room temperature. The specimen was then kept in an excess of benzene with 0.1% PBN for 24 h. Finally, the vulcanizate was extracted for 2 h in pure benzene and weighed in swollen state (a_2). The mass of the dried specimen (a_3) was determined after drying for six days at room temperature. From the values of a_1 , a_2 , and a_3 , V_r was calculated as before and the concentration of chemical crosslinks was determined.

2.4 Determination of Concentration of Crosslinks after the Cleavage of Polysulphidic and Disulphidic Crosslinks^{7,8}

The specimen weighing about 0.2 – 0.3 g (a_1) was allowed to stand in 100 ml of 1-hexane thiol in piperidine (1 M solution) containing 0.5% PBN for 48 h at room temperature. The mixture was agitated occasionally. 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. Then the specimen was kept in an excess of benzene with 0.1% PBN for 24 h. After that the specimen was kept in pure benzene for 2 h 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.

2.5 Determination of the Amount of Free Sulphur and Sulphide Sulphur

Free sulphur was determined iodometrically by converting it to sodium thiosulphate according to ASTM D 297-72A. Zinc sulphide sulphur was determined iodometrically from the formation of cadmium sulphide as described in BS 902 Pt. 1310 – 1958.

2.6 Determination of Mechanical Properties

The compounds were vulcanized up to the respective optimum cure times in a steam heated laboratory press. The tensile properties of the vulcanizates were determined according to ASTM D412 (1980) using dumb-bell specimens at 28 °C at a cross-head speed of 500 mm/min 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 samples at 100 °C for 48 h in an air oven and then measuring the retention in these properties.

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3. Results and Discussion

3.1 Cure Characteristics

When the amount of CBS is increased at constant sulphur level, the vulcanization becomes faster as evidenced in the decrease in the cure times (Tab. 1). Increasing the amount of sulphur, keeping the amount of CBS constant, also speeds up vulcanization. However, the increase in cure rate in this case is not as pronounced as in the previous case. The maximum torque, a measure of the crosslink density, increases steadily with increase of sulphur and/or CBS. Since SBR is likely to take more time for curing using the formulations employed in the study, the curing behaviour of the 50/50 NR/SBR blend seems to be more or less that of NR alone. This might be because the NR phase takes a larger share of the curatives and hence the state of cure in the SBR phase might not be optimum. However, the presence of SBR seems to give very good reversion resistance to the blend since none of the mixes shows any tendency for reversion.

3.2 Network Structure

Tab. 2 shows the results of the chemical characterization of the vulcanizates. The total crosslink density increases with increase in sulphur and/or accelerator. Vulcanizates with comparatively higher amounts of sulphur and lower amounts of accelerator are found to have a larger percentage of polysulphidic crosslinks. The proportion of monosulphidic linkages in the vulcanizates could be determined by the method outlined in section 2.4, assuming carbon-carbon linkages to be negligible. However, this estimation was found to be difficult in the vulcanizates before ageing since the samples got dissolved in the solvent partly after treatment with the reagent, obviously due to the very low concentration of monosulphidic linkages. Hence the proportion of disulphidic linkages which could be obtained by subtracting the proportions of poly- and monosulphidic linkages from the total crosslink density also could not be estimated for the vulcanizates before ageing.

The crosslink density of the vulcanizates is found to increase with ageing. An examination of the percentages of poly-, di-, and monosulphidic linkages of the vulcanizates before and after ageing indicates that the increase in crosslink density might be due to a fraction of the polysulphidic linkages getting shortened with additional crosslinking. The variation in the crosslink

Tab. 2. Chemical characterization of the vulcanizates.

Vulcanizate	A	B	C	D	E	F	G	H
Total crosslink density $\left(\frac{\text{m} \cdot \text{mol}}{\text{kg RH}}\right)^a$	42.03	46.32	56.81	70.01	40.65	47.15	52.12	58.52
Polysulphidic cross-links (%)	62.0	66.32	72.73	78.57	66.02	64.33	63.21	62.32
Monosulphidic cross-links (%)	b	b	b	b	b	b	b	b
Free sulphur concentration	21.25	26.58	39.67	48.69	28.82	22.81	20.42	18.77
Zinc sulphide sulphur concentration	34.35	35.66	42.28	50.02	35.90	33.80	30.50	28.29
After ageing								
Total crosslink density $\left(\frac{\text{m} \cdot \text{mol}}{\text{kg RH}}\right)$	58.85	62.63	74.83	90.51	57.42	66.72	72.32	85.78
Polysulphidic cross-links (%)	54.83	55.12	56.25	58.16	55.21	52.34	51.18	48.32
Monosulphidic cross-links (%)	18.62	19.12	19.84	20.34	16.32	17.21	18.85	21.25
Free sulphur concentration $\left(\frac{\text{m} \cdot \text{mol}}{\text{kg RH}}\right)$	8.90	11.40	17.45	21.91	9.49	6.84	5.54	4.78

^a Millimole

kilogram of rubber hydrocarbon

^b Exact determination is found to be difficult since the vulcanizate dissolves in the solvent after treatment with the reagent.

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density with ageing increases with higher amounts of sulphur or accelerator in the original mix. This might be due to a larger proportion of polysulphidic crosslinks being available for shortening in the former case, whereas in the latter case it might be due to a higher amount of accelerator⁶.

The amount of combined sulphur in the vulcanizates may be taken as the amount of sulphur added according to the formulation minus the amounts 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 amounts of sulphur but decrease with increasing amounts of accelerator in the original mix. Whereas the amount of zinc sulphide sulphur remains more or less constant with ageing, part of free sulphur gets used up in further crosslinking at the time of ageing.

3.3 Mechanical Properties

Except tensile strength (Fig. 1 and 2) other properties show a definite relationship with crosslink density. Elongation at break (Fig. 3 and 4) decreases with increase in crosslink density whereas modulus (Fig. 5 and 6) and hard-

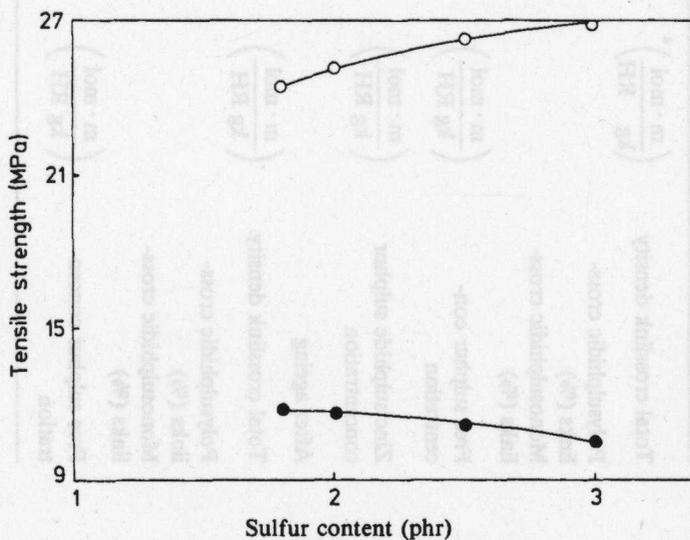


Fig. 1. Variation of tensile strength with sulfur content; ○ before ageing; ● after ageing.

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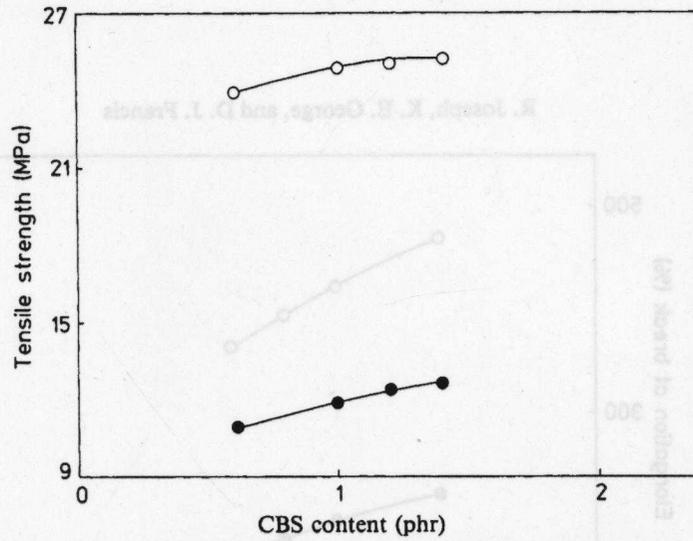


Fig. 2. Variation of tensile strength with CBS content; ○ before ageing; ● after ageing.

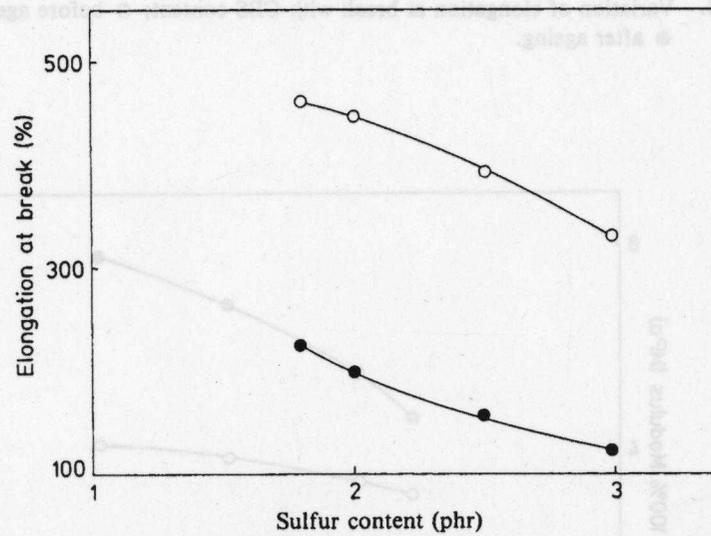


Fig. 3. Variation of elongation at break with sulfur content; ○ before ageing; ● after ageing.

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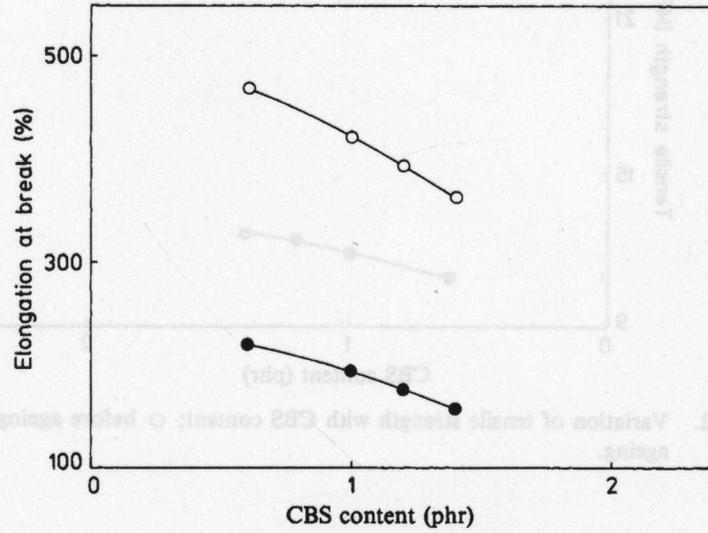


Fig. 4. Variation of elongation at break with CBS content; ○ before ageing; ● after ageing.

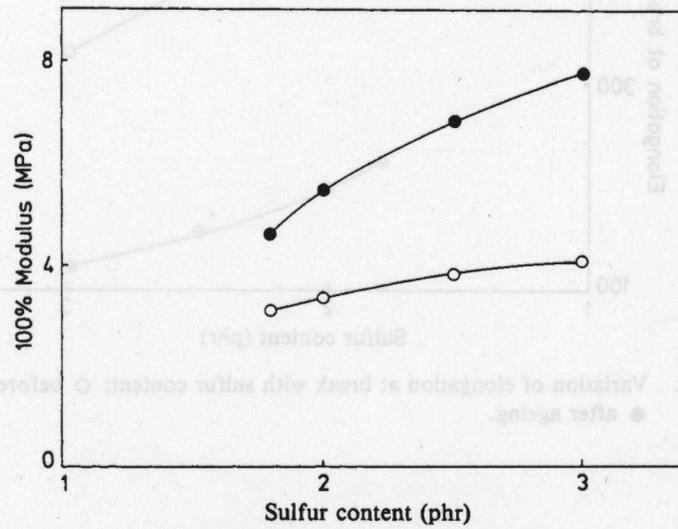


Fig. 5. Variation of modulus with sulfur content; ○ before ageing; ● after ageing.

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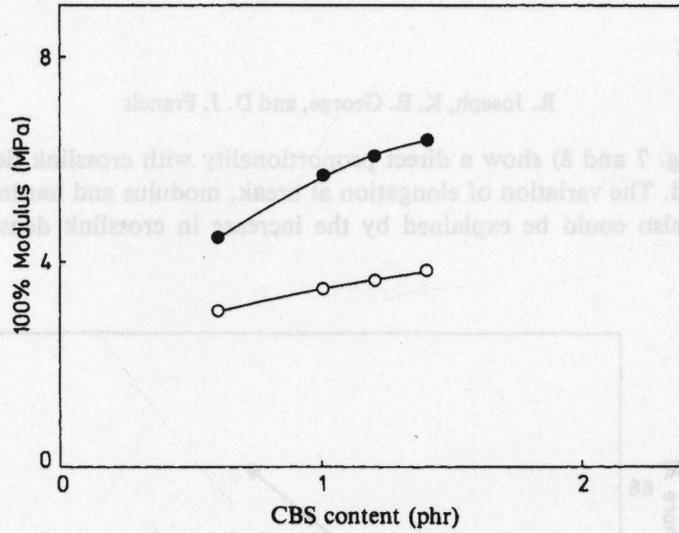


Fig. 6. Variation of modulus with CBS content; ○ before ageing; ● after ageing.

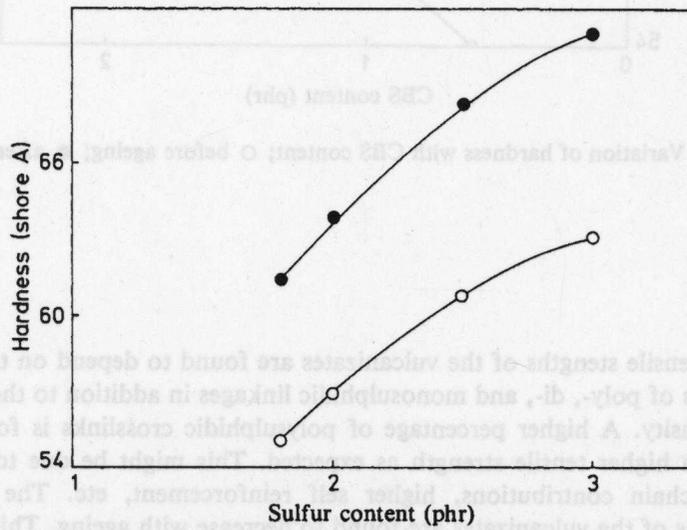


Fig. 7. Variation of hardness with sulfur content; ○ before ageing; ● after ageing.

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ness (Fig. 7 and 8) show a direct proportionality with crosslink density as expected. The variation of elongation at break, modulus and hardness with ageing also could be explained by the increase in crosslink density with ageing.

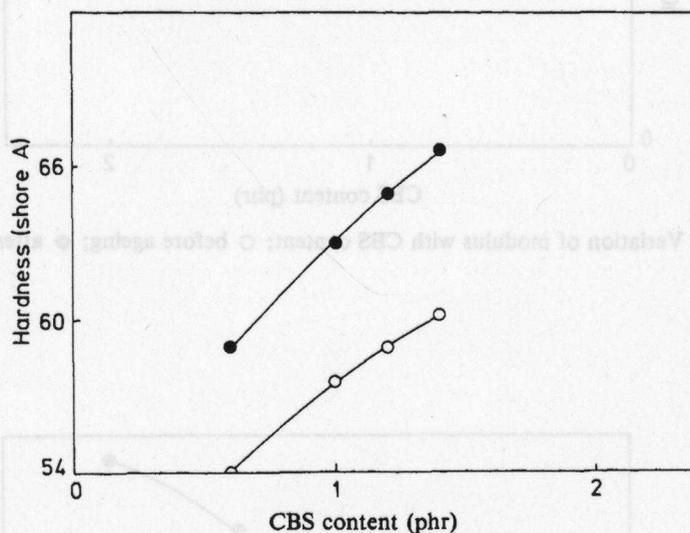


Fig. 8. Variation of hardness with CBS content; ○ before ageing; ● after ageing.

The tensile strengths of the vulcanizates are found to depend on the proportions of poly-, di-, and monosulphidic linkages in addition to the crosslink density. A higher percentage of polysulphidic crosslinks is found to result in higher tensile strength as expected. This might be due to larger elastic chain contributions, higher self reinforcement, etc. The tensile strengths of the vulcanizates are found to decrease with ageing. This might be due to the decrease in the concentration of polysulphidic crosslinks and due to other factors such as main chain scission occurring during ageing. The vulcanizates with less amount of sulphur and more accelerator are generally found to display higher ageing resistance which might indicate that monosulphidic linkages are more resistant to ageing than polysulphidic linkages.

4. Conclusions

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

(1) Formulations with different conventional vulcanizing systems show good resistance to reversion.

(2) The total crosslink density and the proportions of mono-, di-, and polysulphidic linkages in the vulcanizates could be estimated by chemical probes.

(3) The single most important factor in determining the mechanical properties of the vulcanizates is the degree of crosslinking. Properties like tensile strength are also strongly influenced by the proportions of mono-, di-, and polysulphidic linkages, but mainly by ageing.

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