

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

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Synopsis

Blends of 50/50 natural rubber (NR) and styrene-butadiene rubber (SBR) are vulcanized using several conventional and semi-EV systems. The cure characteristics and vulcanizate properties are compared. The quantity and quality of crosslinks in each case are deciphered by chemical probes to correlate them with the vulcanizate properties.

INTRODUCTION

Known elastomers do not exhibit all the properties desired, and so, are often blended with a second elastomer during processing. About 75% of all elastomers are used as blends rather than alone. Ethylene-propylene rubber (EPDM) is added to elastomer formulations for improved oil acceptance and ozone resistance, acrylonitrile-butadiene rubber (NBR) for improved oil resistance, chloroprene rubber (CR) for improved flame resistance, polybutadiene (BR) for improved low temperature flexibility, butyl rubber (IIR) for improved gas impermeability, and so on.¹

The largest use of elastomer blends is in the manufacture of tires. Styrene-butadiene rubber (SBR) has better crack resistance, wet grip, and weather resistance than natural rubber (NR) and NR compared to SBR has better strength and lower heat build up and shows better performance at low temperature. Hence, blends of NR and SBR are used extensively in tire manufacture.² However, no definite rules are available for designing a compound for an NR/SBR blend for achieving a set of vulcanizate properties. At present, compounds are designed based on the rule of thumb that SBR requires less sulfur and more accelerator than NR because of the lower unsaturation of SBR.³⁻⁵

A general division can be made in the vulcanization systems used for rubber compounds, as conventional systems which contain a much higher concentration of sulfur than accelerator, and efficient vulcanization (EV) systems in which the concentration of sulfur is considerably lower than that of accelerator.⁶ Vulcanization systems of intermediate composition between EV and conventional systems are often referred to as semi-EV. The ratio of any given accelerator to sulfur largely determines the types of sulfur crosslinks. Lower ratios favor polysulfidic crosslinks and high ratios lead to crosslinks that are predominantly monosulfidic. Monosulfidic crosslinks are more heat stable than polysulfidic crosslinks and hence EV systems give greater heat aging resistance and reversion resistance than do conventional systems. However,

physical properties such as tensile strength and fatigue resistance are better in conventional systems. In this study a 50/50 NR/SBR blend is cured using several conventional and semi-EV systems and the cure characteristics and vulcanizate properties are compared. In each case, the amounts of free sulfur and sulfur existing as zinc sulfide are estimated to get a feeling of the amount of combined sulfur. The crosslink density and the relative amounts of mono-, di-, and polysulfidic linkages are also assessed to correlate them with the vulcanizate properties.

EXPERIMENTAL

Determination of Cure Characteristics

The formulations of the conventional system and their cure characteristics are given in Table I and those of the semi-EV system in Table II. The compounds were prepared on a laboratory mixing mill. NR/SBR blend was made initially and then the other additives followed in the usual order. The cure characteristics of the mixes were determined at 150°C on a Monsanto rheometer model R.100.

Determination of Technical Properties

The compounds were vulcanized up to the respective optimum cure times on a steam-heated laboratory press. The tensile properties of the vulcanizates were determined according to ASTM D412 (1980) using dumb-bell specimens at 25°C at a crosshead speed of 500 mm/min with a Zwick universal testing machine. Compression set and hardness were determined according to ASTM D395 (1969) and ASTM 2240 (1968), respectively. Aging resistance was determined by maintaining the samples at 100°C for 48 h in an air oven and then measuring the retention in the technical properties.

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

Vulcanizate samples weighing 0.2–0.3 g were allowed to stand in excess of benzene containing 0.1% phenyl- β -naphthylamine (PBN). 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 specimen (a_1), of the swollen specimen (a_2), and of the mass of the specimen after drying for 6 days at laboratory temperature (a_3), the volume fraction of rubber in the swollen network (V_r) was calculated according to the relation,⁹

$$V_r = \frac{(a_3 - a_1 \cdot S_1/S_2)1/d\gamma}{(a_3 - a_1 \cdot S_1/S_2)1/d\gamma + (a_2 - a_3)1/d_b}$$

where

S_1 = the sum of the contents of sulfur and zinc oxide (per hundred rubber-phr)

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

$d\gamma$ = density of rubber (average value of NR (915 kg m⁻³) and SBR (940 kg m⁻³) was taken)

d_b = density of benzene (865 kg m⁻³)

TABLE I
Formulations and Cure Characteristics of the Mixes Employing Conventional Curing Systems

Mix	A	B	C	D	E	F	G	H
<i>Formulations</i>								
NR ^a	50	50	50	50	50	50	50	50
SBR ^b	50	50	50	50	50	50	50	50
ZnO	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
CBS ^c	0.8	0.8	0.8	0.8	0.6	1.0	1.2	1.4
Sulfur	1.8	2.0	2.5	3.0	2.0	2.0	2.0	2.0
<i>Cure characteristics</i>								
Scorch time, min	11.0	10.5	10.5	10.5	12.5	12.0	12.0	11.5
Optimum cure time, min	21.0	20.0	19.5	19.5	24.5	18.5	18.0	16.5
Maximum torque, N · m	59.0	63.0	72.0	79.0	60.0	67.0	71.0	74.0
Reversion, number of units dropped in 5 min	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

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

^b23.5% styrene; Mooney viscosity, ML(1 + 4) at 100°C, 49.2.

^cN-cyclohexylbenzothiazyl sulfenamide; Alkali and Chemical Corporation of India Limited.

TABLE II
Formulations and Cure Characteristics of the Mixes Employing Semi-EV Curing Systems

Mix	I	J	K	L	M	N	O	P
<i>Formulations</i>								
NR ^a	50	50	50	50	50	50	50	50
SBR ^b	50	50	50	50	50	50	50	50
ZnO	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
CBS ^c	1.2	1.2	1.2	1.2	1.0	1.25	1.5	2.0
Sulfur	1.2	1.5	1.8	2.1	1.6	1.6	1.6	1.6
<i>Cure characteristics</i>								
Scorch time, min	9.5	12.0	12.5	11.0	14.5	14.0	13.5	12.0
Optimum cure time, min	19.5	19.5	18.5	17.5	25.0	21.0	20.5	18.5
Maximum torque, N · m	55.0	66.0	68.0	77.0	61.0	67.0	69.0	73.0
Reversion, number of unit dropped in 5 min	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

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

^b23.5% styrene; Mooney viscosity, ML(1 + 4) at 100°C, 49.2.

^cN-cyclohexylbenzothiazyl sulfenamide; Alkali and Chemical Corporation of India Ltd.

From the value of V_r so obtained the elastic constant C_1 was then calculated from the relation.^{10,11}

$$-\left[\ln(1 - V_r) + V_r + \chi V_r^2\right] = \frac{2C_1 V_s (V_r^{1/3} - V_r/2)}{RT}$$

where χ is a parameter characteristic of interaction between the rubber network and the swelling agent. For NR-benzene system the value of χ could be taken as a constant (0.425) whereas for SBR-benzene system it could be calculated from the relation¹²

$$\chi = 0.330 + 0.43 V_r$$

Since the values of χ for NR and SBR were sufficiently close in most cases, the average value was taken for the blend. V_s is the molar volume of benzene (90 cc/mol), R the gas constant, and T the absolute temperature.

The C_1 value so obtained was converted into the concentration of chemical crosslinks ($2M_{c, \text{chem}}^{-1}$) using the Mullins formula,¹³

$$C_1 = \left[\rho RT(2M_{c, \text{chem}})^{-1} + 0.78 \times 10^6\right] \\ \times \left[1 - 2.3(M_{c, \text{chem}})\bar{M}_n^{-1}\right] \text{ dynes/cm}^2$$

where ρ is the density of the rubber network and \bar{M}_n the number average molecular weight of the rubber before vulcanization. An approximate value of \bar{M}_n for the blend was calculated from the Mooney viscosity of the blend¹⁴ as 1.5×10^5 .

Determination of Concentration of Crosslinks After the Cleavage of Polysulfidic Crosslinks^{7,8}

A 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 28°C. Then the solvent was replaced by a solution of 0.4M solution of propane-2-thiol and piperidine in benzene containing 0.5% PBN for 2 h. On completion of reaction, the sample was removed from the reagent solution, washed with petroleum ether (bp 40–60°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 excess of benzene with 0.1% PBN for 24 h. Finally, the vulcanizate was extracted for 2 h in pure benzene and weighed (a_2). The mass of the 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 Polysulfidic and Disulfidic Crosslinks^{7,8}

A test specimen weighing about 0.2–0.3 g (a_1) was allowed to stand in 100 ml of 1-hexane thiol in piperidine (1M solution) containing 0.5% PBN at 28°C for 48 h. The apparatus was agitated occasionally. On completion of

reaction, the sample was removed from the reagent solution, washed with petroleum ether (bp 40–60°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 kept in excess of benzene with 0.1% PBN for 24 h, after which it was kept in pure benzene for 2 h and weighed (a_2). It was then dried for 6 days at laboratory temperature and weighed (a_3). The concentration of chemical crosslinks was determined as before.

Determination of Amount of Free Sulfur and Sulfide Sulfur

Free sulfur was determined iodometrically by converting it to sodium thiosulfate according to ASTM D 297-72A. Sulfide sulfur was determined iodometrically from the formation of cadmium sulfide as described in BS 902, pt 1310, 1958.

RESULTS AND DISCUSSION

Only gum formulations were selected for study to make the chemical evaluations as realistic as possible. Antioxidants were also not used to study the effect of aging on the raw polymers.

Cure Characteristics

Increasing the amount of CBS at constant sulfur level seems to reduce the scorch safety and to speed up vulcanization both in the conventional and semi-EV systems as expected. However, when the amount of sulfur is varied keeping the amount of CBS constant, no definite pattern of change is visible in the cure characteristics. Lack of a clear pattern in the cure characteristics when the amounts of crosslinking agents are varied might imply that the 50/50 NR/SBR blend is not fully compatible. However, there is not much change in the scorch and cure times within the range of sulfur and CBS variations tried in this study. The maximum torque, which is a measure of the crosslink density, increases steadily with increase of sulfur or CBS both in the conventional and semi-EV system. Unlike the curing of NR, no compound shows any tendency for reversion.

Mechanical Properties

The mechanical properties of the blends are shown in Figures 1–10. Tensile strength of the vulcanizates (Figs. 1 and 2) is found to improve steadily when the amount of sulfur or CBS is increased in both the conventional and semi-EV systems, which might be due to the higher degree of crosslinking induced by them. Vulcanizates of the conventional system generally are found to display higher strength. This might mean a higher concentration of overall chemical crosslinks and polysulfidic crosslinks in the conventional system than the corresponding semi-EV system. Since the crosslink density of the vulcanizates is not likely to decrease with aging, it is clear that changes in crosslink density alone cannot explain the fall in tensile strength of the vulcanizates with aging. The deterioration in tensile strength of the vulcanizates may be principally due to main chain scission.³ There seems to be an optimum crosslink density where the retention in tensile strength is maximum. Other

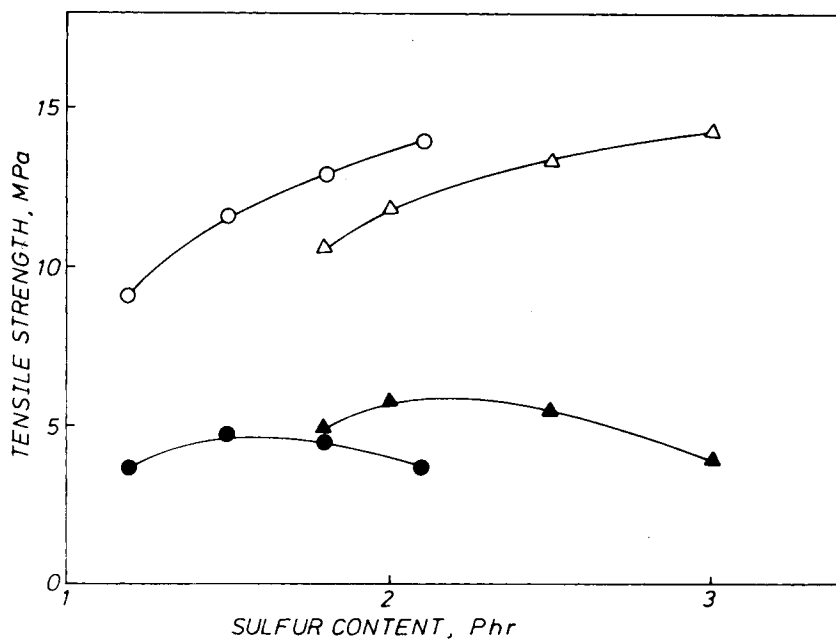


Fig. 1. Variation of tensile strength with sulfur content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

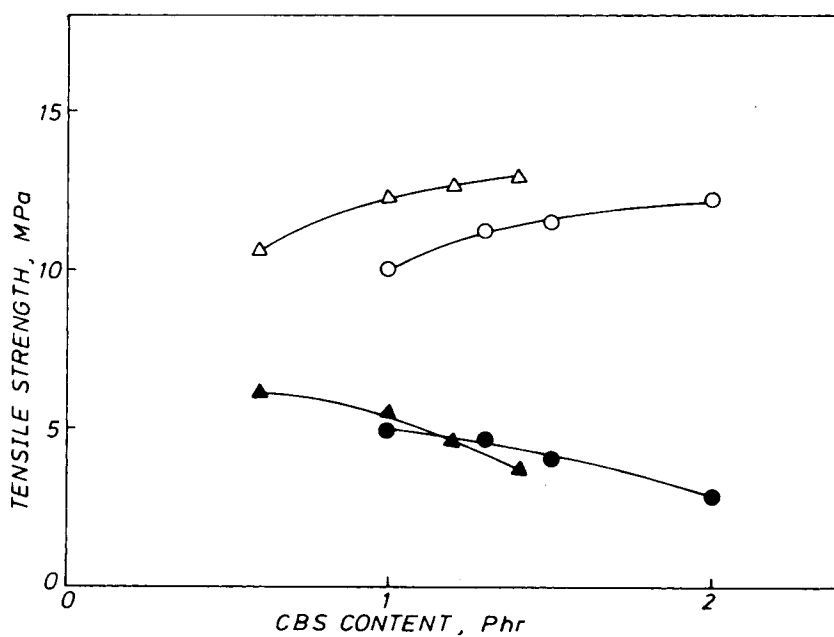


Fig. 2. Variation of tensile strength with CBS content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

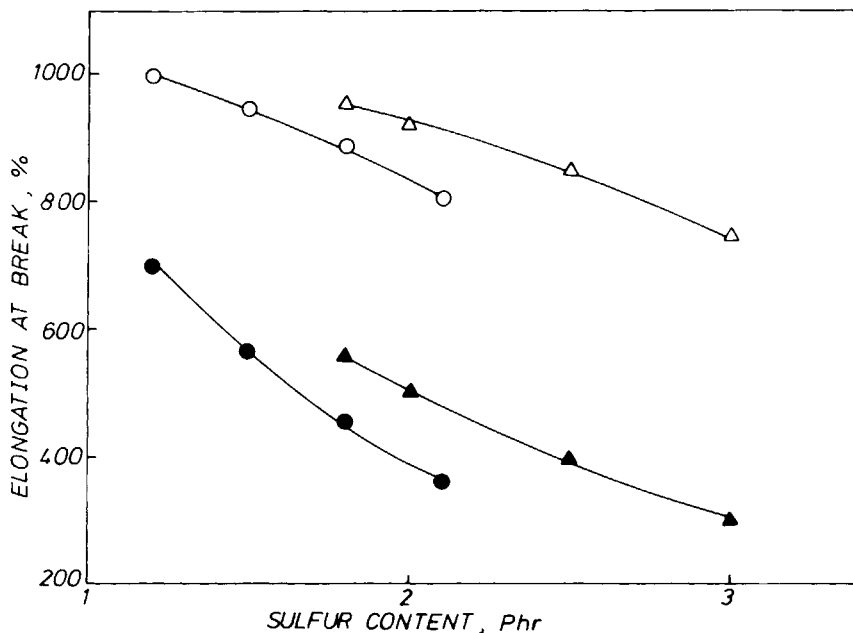


Fig. 3. Variation of elongation at break with sulfur content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

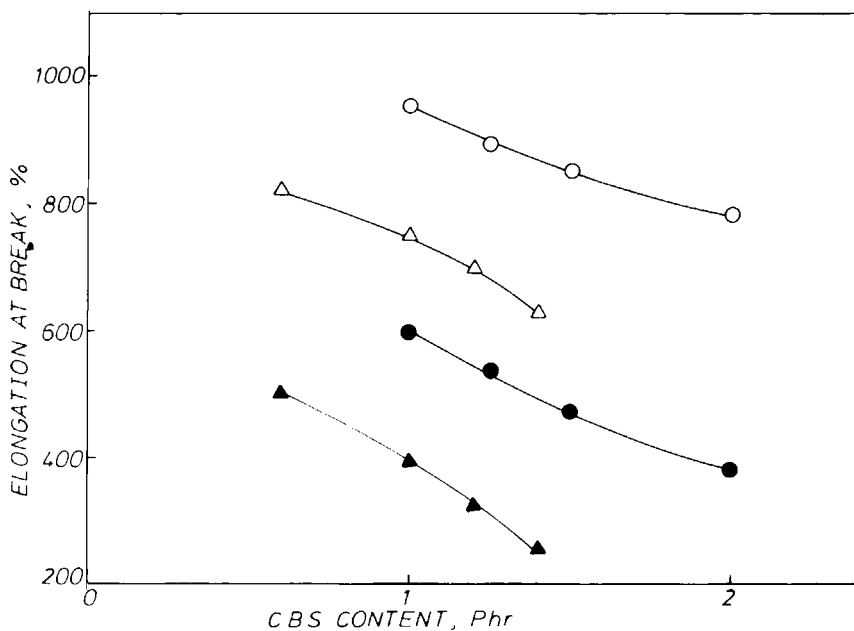


Fig. 4. Variation of elongation at break with CBS content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

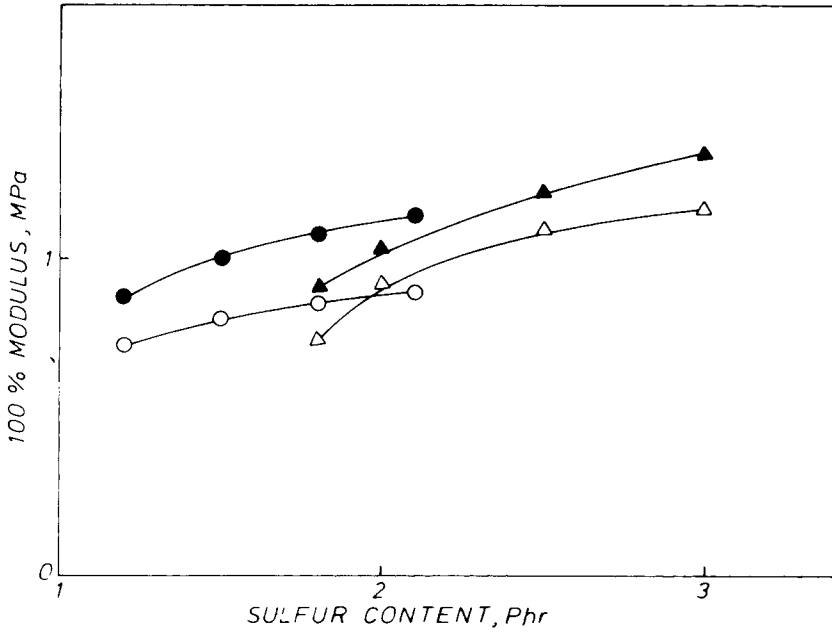


Fig. 5. Variation of modulus with sulfur content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

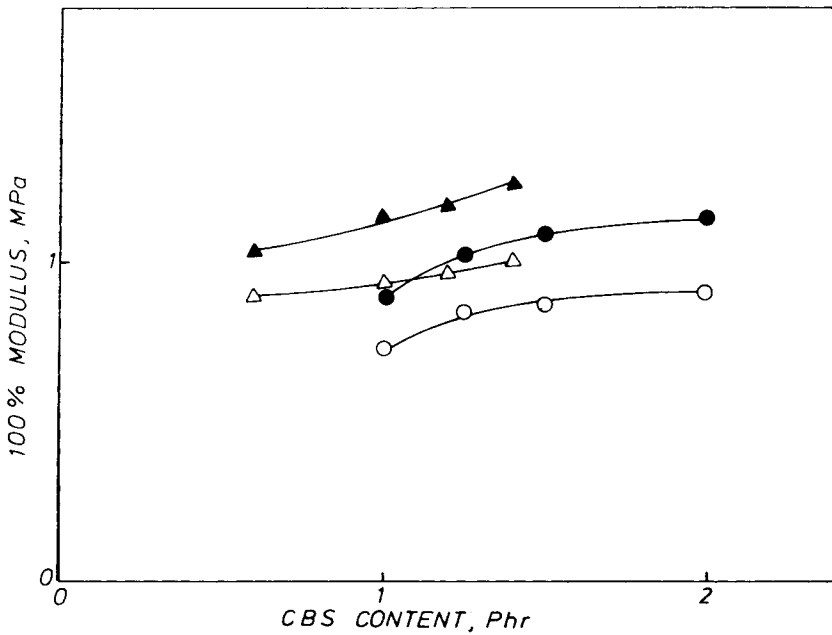


Fig. 6. Variation of modulus with CBS content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

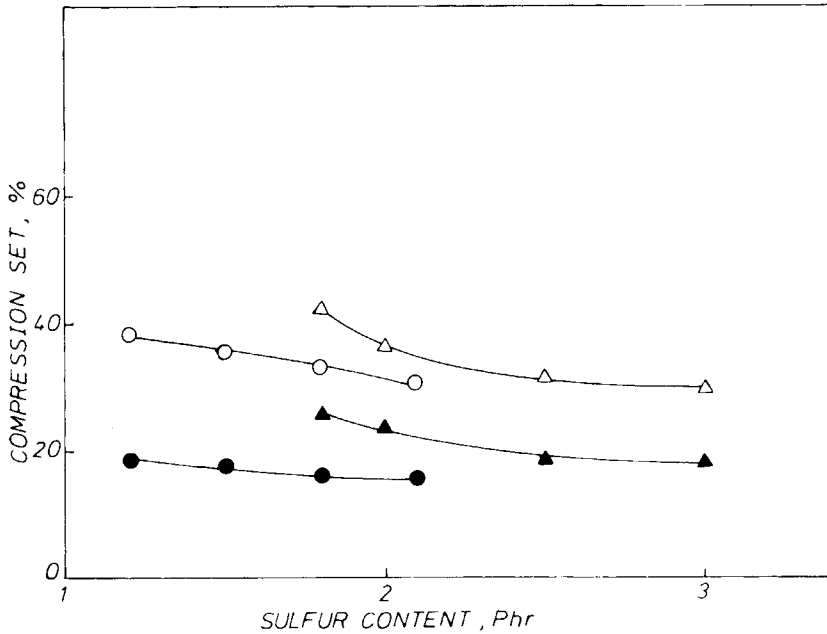


Fig. 7. Variation of compression set with sulfur content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

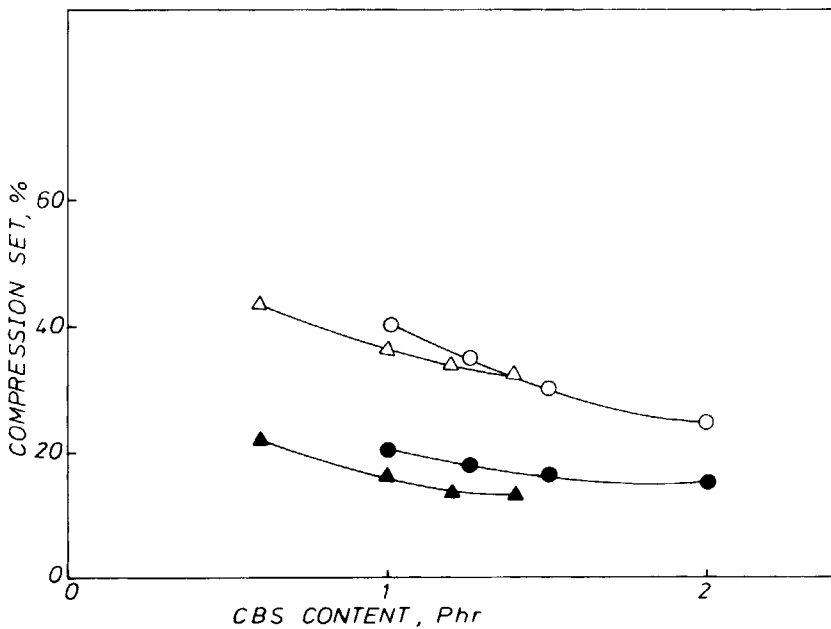


Fig. 8. Variation of compression set with CBS content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

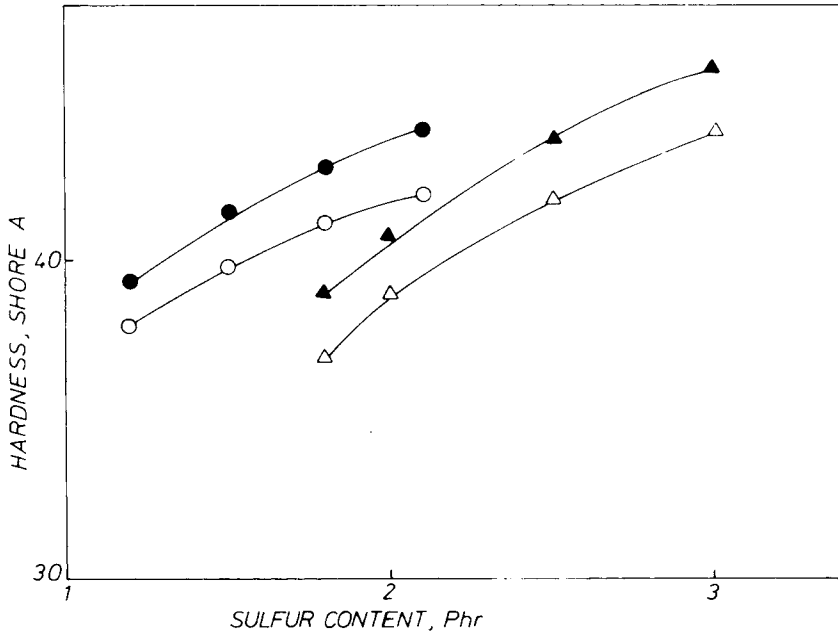


Fig. 9. Variation of hardness with sulfur content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

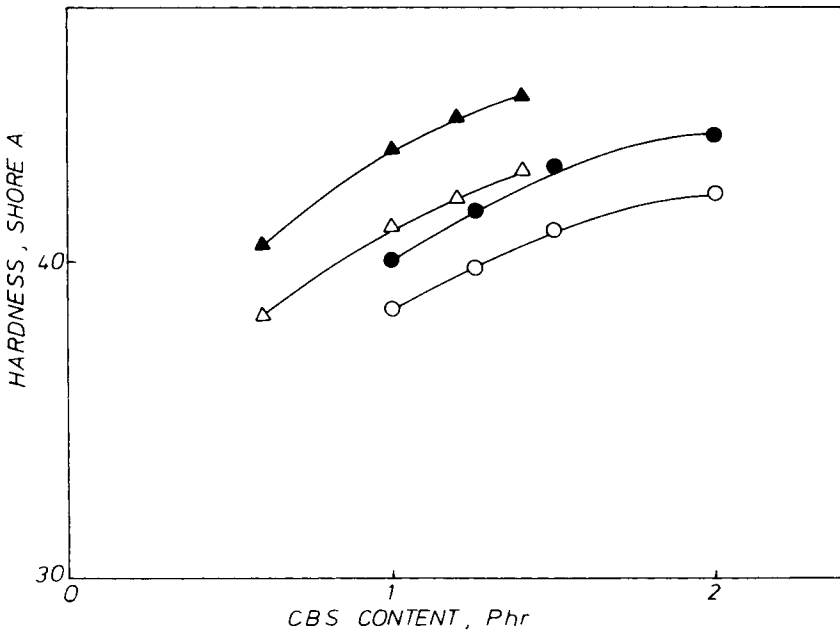


Fig. 10. Variation of hardness with CBS content: (Δ) Conventional system before aging; (\blacktriangle) Conventional system after aging; (\circ) Semi-EV system before aging; (\bullet) Semi-EV system after aging.

mechanical properties, elongation at break (Figs. 3 and 4), modulus (Figs. 5 and 6), compression set (Figs. 7 and 8), and hardness (Figs. 9 and 10) are found to depend mostly on the degree of crosslinking only and not on the nature of crosslinks. Elongation at break decreases with increase in the degree of crosslinking, whereas modulus, compression set, and hardness improve with higher degree of crosslinking. The deterioration in elongation at break and the improvement in modulus, compression set, and hardness with aging might imply that the crosslink density increases further with aging both in the conventional and semi-EV systems.

Network Structure

Table III shows the results of the chemical characterization of the vulcanizates of the conventional system. The crosslink density is found to increase with the addition of sulfur or CBS as expected. It is observed that the polysulfidic crosslinks constitute the major part of crosslinks in this case. The concentration of monosulfidic crosslinks before aging could not be estimated since the vulcanizate sample partly dissolved in benzene after the cleavage of poly- and disulfidic linkages, obviously due to the very low concentration of monosulfidic linkages. However, it is observed that there is a significant conversion from polysulfidic linkages to di- and monosulfidic linkages during aging, which also may be one reason for the decrease in tensile strength with aging. The overall crosslink density is also found to improve with aging as expected. Free sulfur content and the amount of sulfur existing as zinc sulfide increase with higher concentrations of sulfur but decrease with higher concentrations of CBS as expected. Table IV shows the results of the chemical characterization of the vulcanizates of the semi-EV systems. As in the case of the conventional system, the crosslink density increases with increase in the amounts of sulfur or CBS. However, the amount of polysulfidic linkages is much less in this case compared to the conventional system. The concentration of monosulfidic linkages is found to be higher, but its exact determination was found to be difficult to obtain as before. As in the case of the conventional system, there is a significant conversion from polysulfidic linkages to di- and monosulfidic linkages at the time of aging. The variation of free sulfur and zinc sulfide sulfur is similar to that of the conventional system.

CONCLUSIONS

The study helps to draw the following conclusions about the cure characteristics and the vulcanizate properties of 50/50 NR/SBR blend.

1. Compounds of conventional and semi-EV curing systems do not show any tendency for reversion.
2. The tensile strength of the vulcanizates depends on the concentration and nature of crosslinks. Generally, a conventional system produces more strength. Other mechanical properties like elongation at break, modulus, compression set, and hardness depend mostly on the overall crosslink density only.

3. Since the mixes do not show any tendency for reversion, there is no particular advantage in using a semi-EV system. The aging resistance of both the conventional and semi-EV systems is more or less similar.
4. The crosslink density and the percentage of polysulfidic linkages is generally higher in a conventional system compared to those of a semi-EV system.
5. The crosslink density increases at the time of thermal aging both in the conventional and semi-EV system. At the same time, a large fraction of the polysulfidic linkages gets converted into di- or monosulfidic linkages.
6. The amount of zinc sulfide sulfur does not vary much with aging. But a part of the free sulfur is found to take part in crosslinking at the time of aging.

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