Effect of Curing Temperature and Curing System on Network Structure and Technical Properties of Polybutadiene and Styrene–Butadiene Rubber

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Synopsis

The effect of curing temperature and curing system on the network structure and technical properties of polybutadiene (BR) and styrene–butadiene rubber (SBR) has been studied. The technical properties have been correlated with the network structure. For example, better dynamic properties like resilience, heat buildup, and set values of the efficiently vulcanized BR system can be ascribed to lower sulfur inefficiency and simpler network structure. Again, higher compression set values of the SBR mixes are due to lower crosslink density and higher proportion of polysulfidic crosslinks.

INTRODUCTION

In our early articles,[1–5] we reported the effect of high-temperature vulcanization on the network structure and properties of natural rubber vulcanizates and rubber blends. Synthetic rubbers are generally vulcanized at higher temperature. But an increase in curing temperature changes the network structure, which in turn may affect the technical properties. In the present article, we report results of our studies on the effect of curing temperatures (150 and 180°C) and curing systems (conventional and efficient vulcanization) on the network structure and technical properties of styrene–butadiene rubber (SBR) and polybutadiene rubber (BR).

Previously, some preliminary studies have been made in this field. The influence of elevated temperature on polyisoprene (IR) and BR in unfilled compound was studied using tetramethyl thiuram disulfide, diphenyl guanidine, and *N*-morpholino-thio-2-benzothiazole as accelerators.[6] Tarasova, Fedorova, and Dogadkin[7] reported the effect of vulcanization temperature (133–200°C) on the properties and vulcanizate structure of oil-extended SBR and IR. Heating at a temperature above 173°C causes unsaturation of the rubber to be greatly reduced. Smith[8] reported differences existing between elastomers and curing systems in respect to high-temperature curing. Elastomers included in the study were natural rubber (NR), SBR, a blend of NR and SBR, butyl rubber, nitrile rubber, and chloroprene rubber. Within the range of temperature studied (145–260°C), an increase in the vulcanization temperature exerted a deleterious effect on the sulfur-cured vulcanizates of all elastomers. Glanville, Milner, and Windibank[9] showed that the presence of BR in blends of NR and BR reduces the degradation of NR vulcanizates cured at high temperature. Blow and Loo[10] observed that the increase in curing temperature caused a decrease in physical

TABLE I
Composition of the Mixes

Mix system	I SBR–EV[e]	J SBR–CON[e]	K BR–EV	L BR–CON
Polybutadiene rubber[a]	—	—	100	100
Styrene–butadiene rubber[b]	100	100	—	—
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
HAF black	50	50	50	50
Processing oil	5	5	5	5
Sulfur	0.5	2	0.5	2
DTDM[c]	1.0	—	1.0	—
CBS[d]	2.0	0.8	2.0	0.8

[a] Cisamer 1203 containing 96% cis-polybutadiene, obtained from Indian Petrochemicals Corp. Ltd., Gujrat.
[b] SBR-1502, obtained from Synthetics and Chemicals Ltd., Bareilly.
[c] Dithiodimorpholine, obtained from Monsanto Co., Akron, OH.
[d] Cyclohexyl benzothiazyl sulfenamide, obtained from Alkali and Chemical Corp. of India Ltd., Rishra, India.
[e] CON stands for conventional system and EV means efficient vulcanization system.

properties and a lowering of crosslink density of vulcanizates based on NR, SBR, and their blends. Howard and Wilder[11] studied the effect of curing temperature on the tread wear of vulcanizates containing controlled microstructured 85/15 butadiene–styrene solution copolymer. Lloyd[12] reported the use of a sulfur donor (4,4′dithiodimorpholine) in combination with sulfenamide as a versatile curing system to exactly suit a wide range of injection molding conditions without any loss of physical properties.

EXPERIMENTAL

The mix formulations are given in Table I and the curing characteristics are reported in Table II. Method of sample preparation was the same as described earlier.[3] The samples were cured to the respective optimum cure times as determined by Monsanto rheometer (R-100). Details of the testing procedures and determination of the network structure were described earlier.[3]

TABLE II
Curing Characteristics of Different Mixes

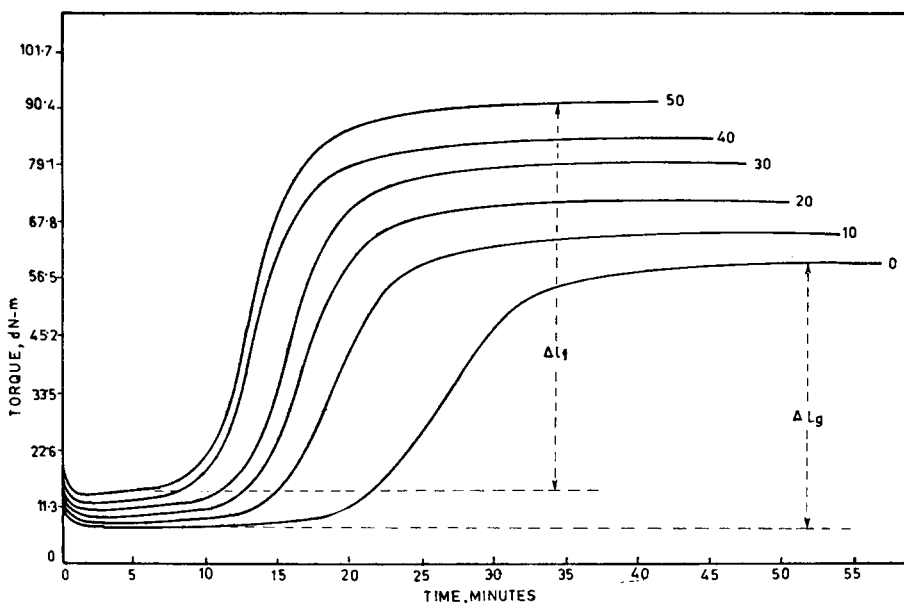| Mix system	I SBR–EV	J SBR–CON	K BR–EV	L BR–CON
Mooney scorch time, t_5, at 120°C, min	52	41	31.5	24.5
Optimum cure time at 150°C, min	18.2	22.0	14.5	13.5
Optimum cure time at 180°C, min	3.9	5.0	3.1	3.5
Maximum rheometric torque, N·m				
(a) 150°C	9.15	10.06	12.43	9.49
(b) 180°C	7.40	8.81	11.07	8.93
Cure rate, % min^{-1}				
(a) 150°C	9.3	6.1	13.3	11.8
(b) 180°C	55.5	23.2	83.3	53.3

Fig. 1. Rheographs of HAF-filled SBR at different loadings at 150°C.

Polymer-filler interaction was studied by equilibrium swelling in benzene and examined by estimating the parameter, C, in the Kraus equation[13]:

$$m - v_{ro} = 3C(1 - v_{ro}^{1/3}) - 1 \qquad (1)$$

where m is obtained from the slope of the plot of v_{ro}/v_{rf} against $\phi/(1 - \phi)$:

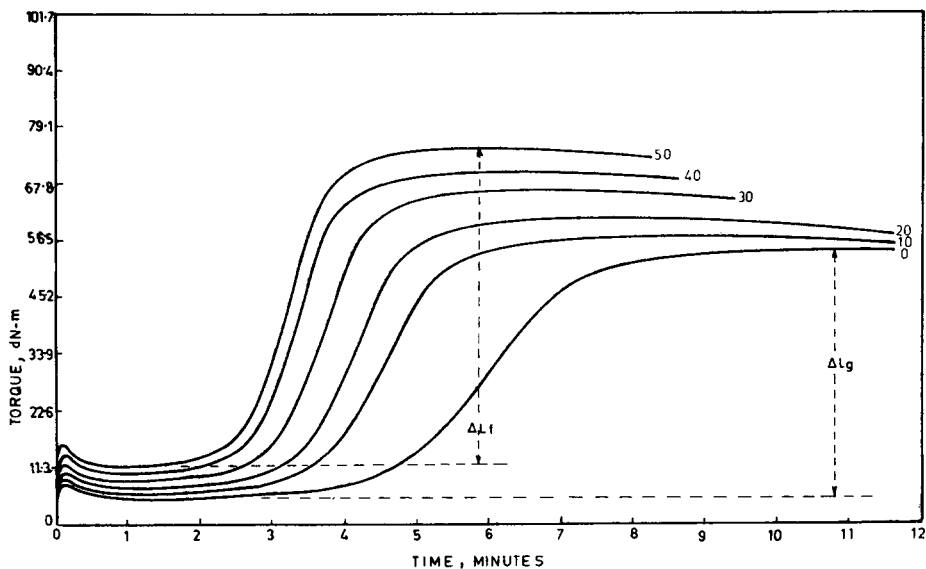$$\frac{v_{ro}}{v_{rf}} = 1 - m \frac{\phi}{1 - \phi} \qquad (2)$$

Fig. 2. Rheographs of HAF-filled SBR at different loadings at 180°C.

TABLE III
Physical Properties of Different Mixes[a]

Curing temp., °C	Mix	System	Tensile strength, MPa	Tear strength, kN/m × 10³	300% modulus, MPa	Elongation at break, %	Hardness, Shore A	Compression set, %	Abrasion loss, cm³/1000 rev
150	I	SBR–EV	21.44 (18.25)	5.41 (4.58)	7.98	610 (310)	61 (66)	59.3	0.54 (0.64)
	J	SBR–CON	19.54 (17.10)	4.97 (4.25)	7.47	557 (250)	62 (70)	68.5	0.53 (0.65)
	K	BR–EV	19.11 (9.89)	4.80 (4.09)	10.69	430 (237)	66 (69)	32.8	0.14 (0.13)
	L	BR–CON	15.55 (7.58)	4.15 (3.65)	7.74	540 (200)	65 (69)	39.4	0.06 (0.14)
180	I	SBR–EV	21.09 (13.41)	5.74 (5.01)	7.32	600 (343)	58 (64)	50.3	0.48 (0.60)
	J	SBR–CON	20.47 (17.64)	5.25 (5.61)	11.09	460 (253)	62 (70)	47.5	0.52 (0.67)
	K	BR–EV	17.73 (13.38)	4.87 (3.67)	9.28	450 (280)	65 (69)	35.4	0.10 (0.12)
	L	BR–CON	14.04 (7.30)	4.58 (3.24)	7.45	450 (167)	63 (70)	34.9	0.07 (0.14)

[a] Values in parentheses indicate the results of aging for 96 hr at 70°C.

TABLE IV

Physical Properties of Different Mixes[a]

Curing temp., °C	Mix	System	Crack growth to 12.7 mm	Flex cracking, kc			Resilience, %	Heat buildup, ΔT, °C	Set, % (Goodrich)
				Grade A	Grade C	Failure			
150	I	SBR-EV	19	89	145	219	32.0 (46.3)	42.0 (30.2)	4.8 (1.0)
	J	SBR-CON	4	20	37	47	30.5 (46.6)	44.0 (28.7)	16.7 (1.3)
	K	BR-EV	102	123	245	>600	54.4 (59.0)	24.7 (26.7)	0.6 (0.5)
	L	BR-CON	557	161	290	>600	45.7 (52.8)	21.3 (28.5)	3.4 (1.4)
180	I	SBR-EV	34	12	26	59	33.5 (43.9)	44.0 (38.7)	7.0 (1.4)
	J	SBR-CON	25	14	26	65	35.6 (47.5)	42.6 (30.0)	5.7 (1.2)
	K	BR-EV	15	15	28	66	56.4 (61.0)	22.8 (24.7)	0.8 (0.4)
	L	BR-CON	50	18	30	112	45.1 (53.1)	23.3 (27.4)	4.1 (1.5)

[a] Values in parentheses indicate results after aging for 96 hr at 70°C.

TABLE V

Percent Change in Physical Properties Changing Curing Temperature from 150 to 180°C

Mix	System	Tensile strength	Tear strength	300% modulus	Hardness	Resilience	Heat buildup	Compression set	Abrasion loss	Set
I	SBR-EV	−1.6	+ 6.1	− 8.2	−4.9	+ 4.7	+4.8	−15.2	−11.1	+45.8
J	SBR-CON	+4.8	+ 5.6	+48.5	0	+16.7	−3.2	−30.7	− 1.9	−65.9
K	BR-EV	−7.2	+ 1.4	−13.2	−1.5	+ 3.7	−7.7	+ 7.9	−28.6	+33.3
L	BR-CON	−9.7	+10.4	− 3.7	−3.1	− 1.3	+9.4	−11.4	+16.6	+20.5

TABLE VI
Retention of Physical Properties After Aging[a]

Curing temp., °C	Mix	System	Tensile strength, % retained	Tear strength, % retained	Resilience, % retained	Hardness change
150	I	SBR–EV	85.1	84.6	144.7	+5
	J	SBR–CON	87.5	85.5	152.9	+8
	K	BR–EV	51.7	85.2	108.4	+3
	L	BR–CON	48.7	87.9	115.5	+4
180	I	SBR–EV	63.6	87.3	131.0	+6
	J	SBR–CON	86.2	106.8	133.4	+8
	K	BR–EV	75.5	75.4	108.1	+4
	L	BR–CON	52.0	70.7	117.7	+7

[a] 96 hr aging at 70°C.

here, v_{ro} represents the volume fraction of rubber in the gum vulcanizate and v_{rf} is the volume fraction of rubber in the filled vulcanizate (assuming filler particles do not swell); ϕ is the volume fraction of filler in the filler vulcanizate. While examining Kraus plots, compounds with different loadings of filler were vulcanized at the respective optimum cure times and v_{rf} at each loading was determined by the equilibrium swelling method.

The cure behavior of the filled stocks at two curing temperatures was also examined in terms of Westlinning and Wolff's α_F values[14] defined by

$$\alpha_F = \left(\frac{\Delta L_f}{\Delta L_g} - 1\right)/W \tag{3}$$

where ΔL_f and ΔL_g stand for the maximum torque measured with the filled stock and gum, respectively, while W represents the weight fraction of filler to polymer. Figures 1 and 2 show representative rheographs at different loadings of fillers at 150 and 180°C used for calculations of α_F values.

Since the calculation of chemical crosslink density is less certain for carbon-black-loaded rubber, we have used the parameter V_r, volume fraction of rubber in the swollen gel as a measure of apparent crosslink density. This includes the effect of restriction to swelling by the filler. The proportion of polysulfidic crosslinks in the total crosslink density was determined from V_r of the swollen vulcanizate before and after treatment with a thiol-amine chemical probe.[15] On the basis of sulfur-inefficiency parameter (E) defined earlier,[15] we have introduced a parameter, E_m, modified sulfur-inefficiency parameter defined by $[Sc]/V_r$ where $[Sc]$ is the concentration of network combined sulfur. The higher the value of E_m, the less the amount of sulfur being utilized for crosslinking.

RESULTS AND DISCUSSION

Table II records the curing characteristics of the different mixes. In both conventional and EV systems, the scorch time of the SBR mixes is higher than that of the BR mixes, indicating the difference in activity of the same accelerator system in different rubbers. This is also apparent with optimum cure times, maximum rheometric torque values, and cure rates.

Physical properties of the different mixes are given in Tables III and IV. The

TABLE VII
Chemical Characterization of Filled Vulcanizate Network

Curing temp., °C	Mix	System	Volume fraction of rubber, V_r[b]	Network combined sulfur, [Sc], g/100 g RH	Sulfur ineffi- ciency parameter, E_m, g/100 g RH	Apparent polysulfidic crosslinks, %	Z,[a] %
150	I	SBR–EV	0.209	0.698	3.3	41.6	27.1
	J	SBR–CON	0.212	1.655	7.8	40.1	10.6
	K	BR–EV	0.255	0.678	2.7	31.8	33.1
	L	BR–CON	0.224	1.581	7.1	47.8	11.2
180	I	SBR–EV	0.189	0.617	3.4	25.4	24.5
	J	SBR–CON	0.216	1.688	7.8	31.9	10.8
	K	BR–EV	0.234	0.610	2.6	23.5	30.4
	L	BR–CON	0.212	1.735	8.2	45.3	10.6

[a] Z = crosslinking efficiency/g of available sulfur.
[b] V_r = volume fraction of rubber (V_r)/g of available sulfur.
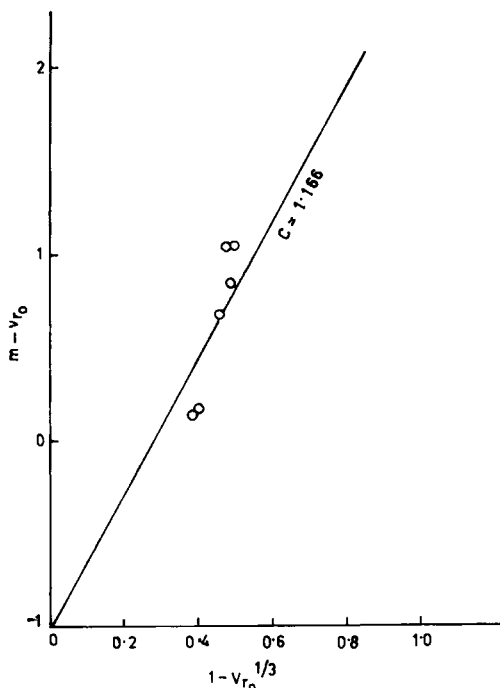
Fig. 3. Plot of $(m - v_{ro})$ vs. $(1 - v_{ro}^{1/3})$ according to eq. (1).

value of the tensile strength is higher in SBR mixes at both curing temperatures. The EV system is better than the conventional one in this respect for both rubbers and at both curing temperatures. Tear-strength values follow similar trend. BR vulcanizates show lower compression set values than SBR vulcanizates. As expected the EV system shows lower set values in all cases. However, elevated curing temperature tends to lower the compression set values. Abrasion resistance and resilience of polybutadiene rubber are excellent. Curing systems and curing temperatures seem to have little effect on abrasion resistance. The resilience is, however, better in the EV mixes. SBR vulcanizate shows higher heat buildup and set (Goodrich). Although curing system and curing temperature seem to have no effect on the heat buildup, the set (Goodrich) is higher in the case of the conventional system.

Changes in the physical properties on changing the curing temperature from 150 to 180°C are reported in Table V. In SBR, the conventional system gives improvements in most properties. On the other hand, the properties of the BR–conventional system deteriorate most on changing the curing temperature from 150 to 180°C.

Percent retention of some of the properties after ageing is given in Table VI (aging properties are reported within the parentheses in Tables III and IV). Strength properties of SBR system are less susceptible to change in ageing than BR. Though the EV system is better in BR mixes, the SBR–conventional system is better than the SBR–EV system.

These properties can be explained on the basis of the characterization of vulcanizate networks (Table II). The value of V_r, volume fraction of rubber in the filled BR–EV system, is greater than in the conventional one at both curing
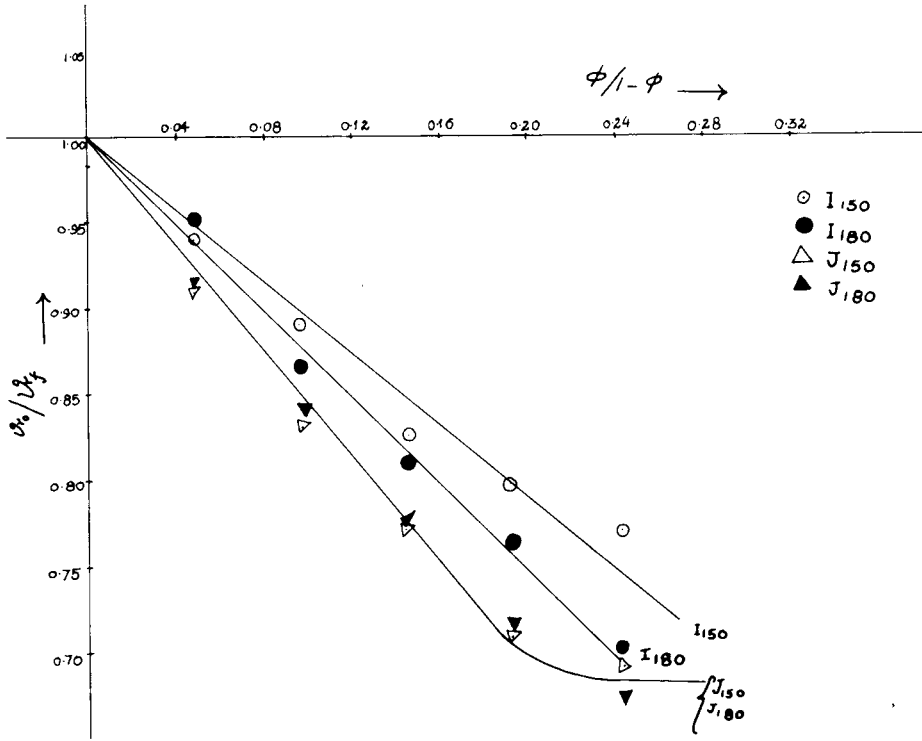
Fig. 4. Plots according to eq. (2) (Kraus plot) for SBR mixes. ⊙, SBR (EV) at 150°C; ●, SBR (EV) at 180°C; △, SBR (CON) at 150°C; ▲, SBR (CON) at 180°C.

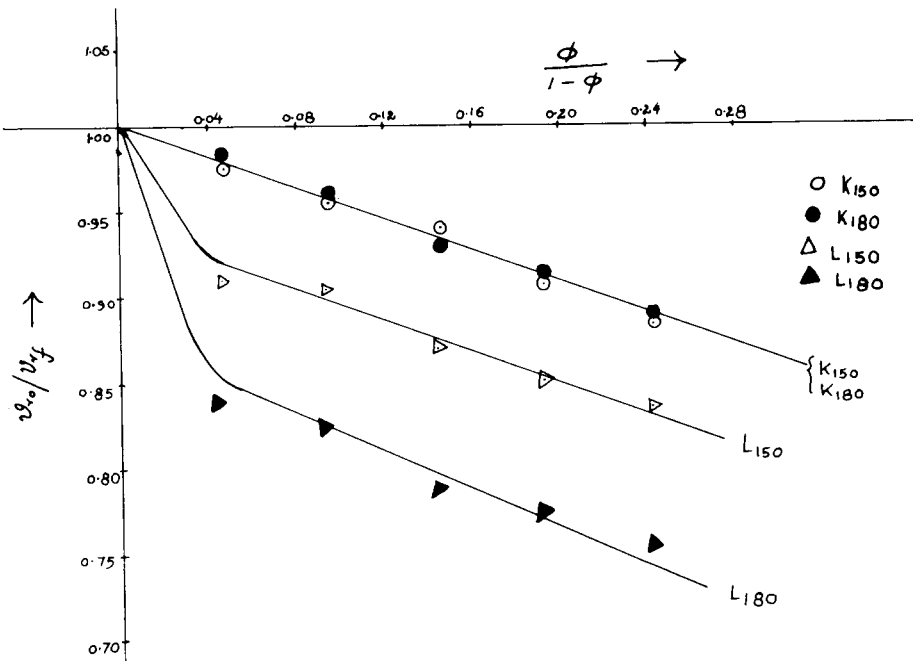

Fig. 5. Plots according to eq. (2) (Kraus plot) for BR mixes. ⊙, BR (EV) at 150°C; ●, BR (EV) at 180°C; △, BR (CON) at 150°C; ▲, BR (CON) at 180°C.
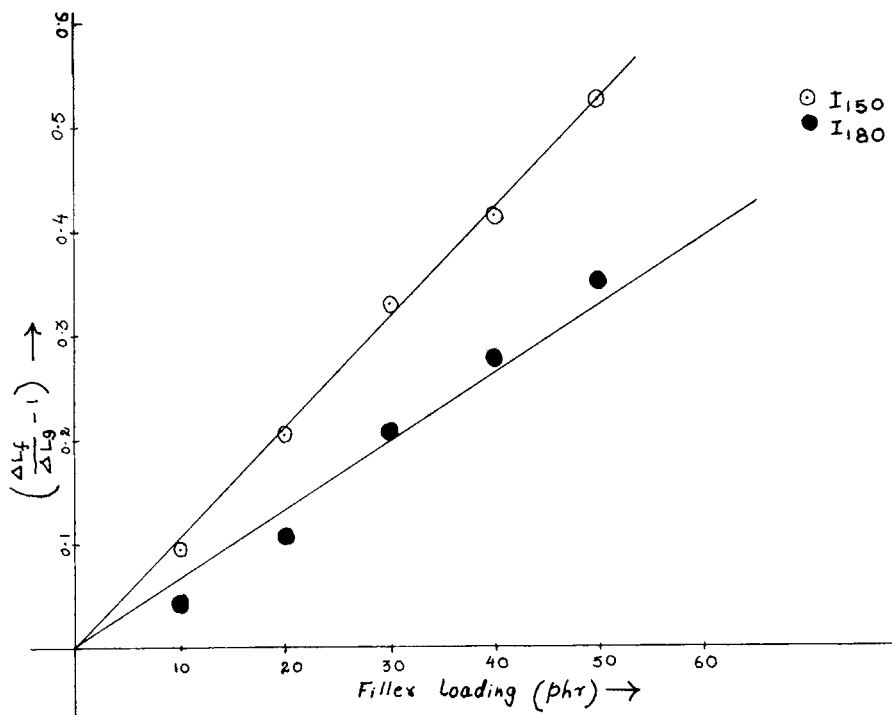
Fig. 6. Plots according to eq. (3) for SBR mixes. ⊙, SBR (EV) at 150°C; ●, SBR (EV) at 180°C.

temperatures. But the conventional system of SBR mixes has higher values of V_r than the EV system. The implied differences in crosslink density can be correlated to [Sc], the network combined sulfur, in the following manner. In the conventional system, though the [Sc] values are higher, the restriction to swelling (indicated by V_r) is less. This means that most of the sulfur is utilized in forming pendant and cyclic sulfides. This is reflected in the sulfur inefficiency parameter, E_m, which is lowest in the case of the BR–EV system. This implies efficient utilization of sulfur and simpler network structure in the BR–EV system.

TABLE VIII
Values of v_{ro}, m, ΔL_g, and α_F

Curing temp., °C	Mix	System	v_{ro}	m eq. (2)	ΔL_g	α_F eq. (3)
150	I	SBR–EV	0.161	0.84	53	1.07
	J	SBR–CON	0.148	1.23	59	1.05
	K	BR–EV	0.225	0.36	80	0.62
	L	BR–CON	0.187	a	72	a
180	I	SBR–EV	0.144	1.00	48	0.66
	J	SBR–CON	0.145	1.23	53	0.90
	K	BR–EV	0.208	0.36	74	0.60
	L	BR–CON	0.160	a	70	0.21

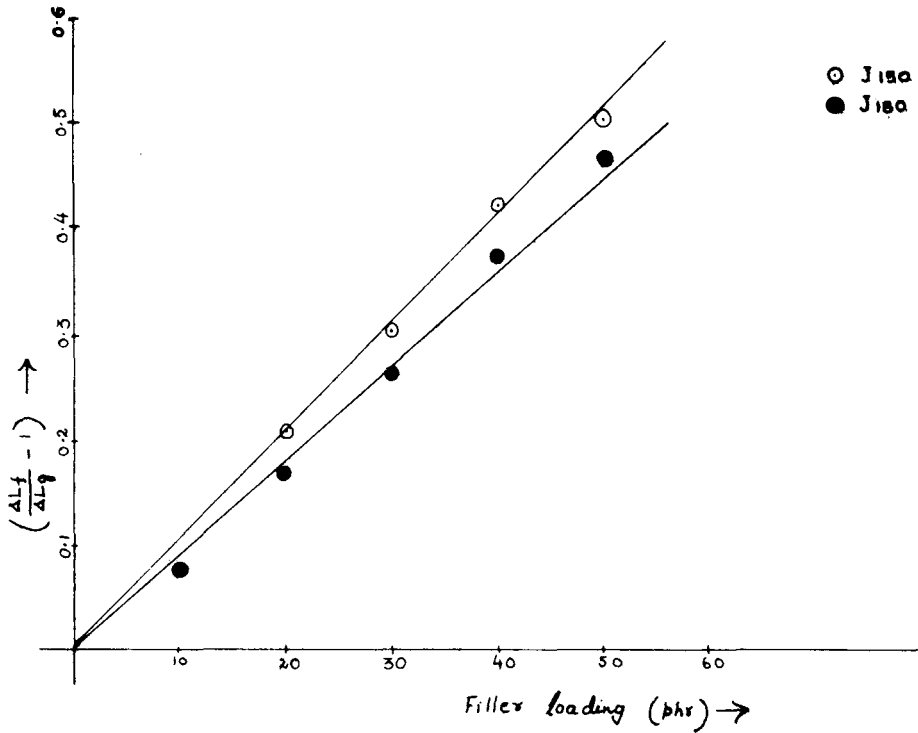a This system does not obey the eqs. (2) and (3).

Fig. 7. Plots according to eq. (3) for SBR mixes. ⊙, SBR (CON) at 150°C; ●, SBR (CON) at 180°C.

This also explains why the dynamic properties like resilience, heat buildup, and set are better in the case of efficiently vulcanized BR. The value of Z, cross-linking efficiency/g of available sulfur, is also higher in the case of all EV mixes
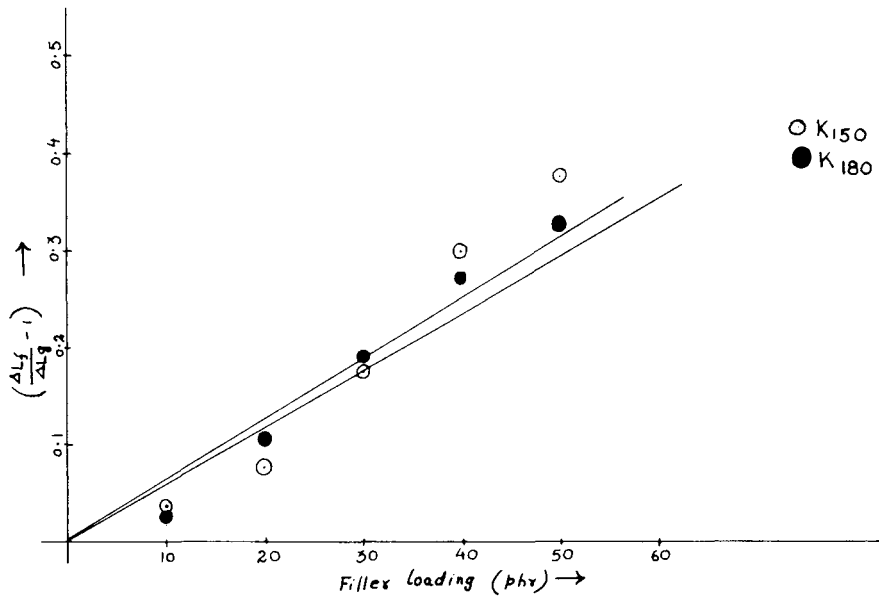

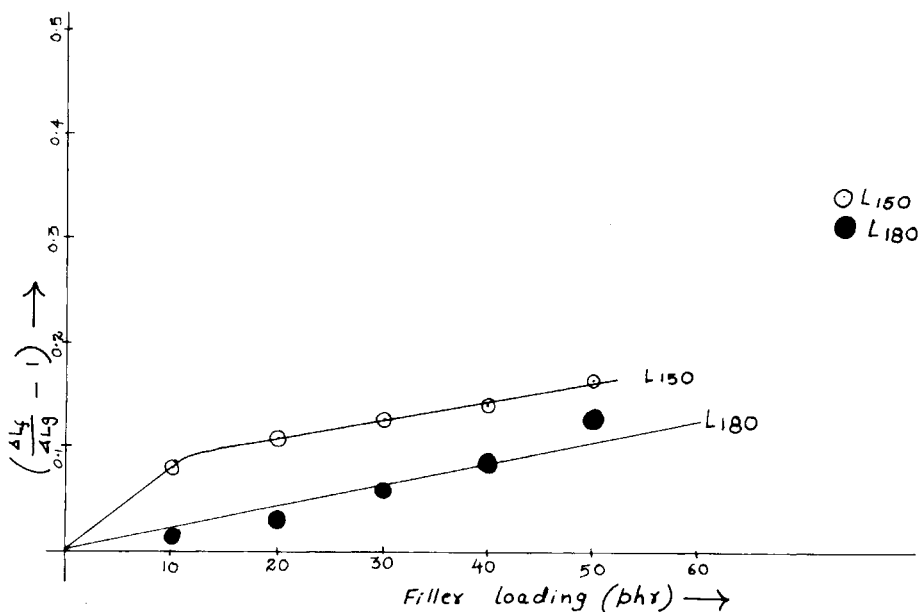Fig. 8. Plots according to eq. (3) for BR mixes. ⊙, BR (EV) at 150°C; ●, BR (EV) at 180°C.

Fig. 9. Plots according to eq. (3) for BR mixes. $\odot$, BR (CON) at 150°C; $\bullet$, BR (CON) at 180°C.

studied and particularly in the BR–EV system. Higher compression set values of the SBR mixes are due to lower crosslink density and higher proportion of polysulfide crosslinks.

As shown in Table VII, the value of percent "apparent" polysulfidic crosslinks is interesting. For BR mixes, the conventional system yields higher polysulfide concentration. In the case of SBR mixes, however, the concentration of poly-sulfidic crosslinks is the same in both curing systems. It seems that the concept of EV and conventional systems, as used in NR vulcanizates, loses its significance in the black-filled SBR mixes. This is reflected in technical properties like re-silience, heat buildup, flex resistance, and tensile strength. Abrasion resistance is related to heat buildup. It seems that frictional properties of polymer rather than the network structure become important in this case. Scanning electron microscopy studies of the abraded surface have indicated that the wear mecha-nism is different in the two rubbers.[16]

To examine the nature of polymer–filler interaction, we have plotted $(m - v_{ro})$ vs. $(1 - v_{ro}^{1/3})$ [eq. (1)]. It is obvious from Figure 3 that SBR– conventional and EV systems and BR–EV system satisfy the Kraus equation, giving $C = 1.166$, quite close to the value of $C = 1.17$ as found by Kraus.[13] It is apparent, therefore, that the polymer–filler interaction is not influenced by the nature of the polymer, curing system and curing temperature. The variation in m (Figs. 4 and 5) is due to the variation in v_{ro} as shown in Table VIII. In the case of the BR–conventional system, the variability in α_F (Figs. 6–9, and Table VIII) clearly suggests the ac-celerating effect of carbon black on the vulcanization, since the carbon black morphology is constant in our present study. Figure 5 shows that the Kraus equation is not obeyed by the BR–conventional system at both curing temper-atures, because v_{ro} can no longer be identified with the swelling of the unfilled stock. A similar observation has also been made by Kraus[13] on the activation

of vulcanization by HAF black in the polybutadiene/sulfur/N-oxydiethylene benzothiazole-2-sulfenamide system. Variability in α_F and scatter of points in the plot of $(m - v_{ro})$ vs. $(1 - v_{ro}^{1/3})$ (Fig. 3) indicate that reinforcing fillers like HAF black might affect the vulcanization processes and crosslink yields.

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