

# Effect of Vulcanization Temperature on the Technical Properties of NR, SBR, and BR

THOMAS KURIAN and K. E. GEORGE, *Department of Polymer Science & Rubber Technology, Cochin University of Science & Technology, Cochin-682022, India*

## Synopsis

Compounds of natural rubber, styrene-butadiene rubber, and butadiene rubber are vulcanized at different temperatures and the crosslink density and physical properties of the vulcanizates are compared. It is found that for each compound there is an optimum vulcanization temperature which results in the best compromise of properties for specific applications.

## INTRODUCTION

Successful rubber technology depends largely on the ability to control the vulcanization process. There should be enough delay of crosslink formation to allow for shaping, forming, etc., and then vulcanization should occur in the final molded shape as rapidly as possible for economic reasons.<sup>1</sup> One way of doing this is to increase the vulcanization temperature.<sup>2</sup> However, care should be taken to obtain the best possible physical properties. The physical properties of sulfur vulcanizates of diene rubbers depend upon the network structure, which is composed of the degree of crosslinking, crosslink structure, and main chain modifications.<sup>3</sup> Of these the most important determining factor of the physical properties is the crosslink density. However, other factors are also important. For example, in sulfur vulcanizing systems the crosslinks can be carbon-carbon, monosulfidic, disulfidic, or polysulfidic.<sup>4</sup> The di- and polysulfidic species are not only thermally fugitive but are also susceptible to nucleophilic, electrophilic, and free-radical attack and hence they undergo further reactions under most conditions of use. On the other hand, polysulfidic crosslinks are associated with more strength.<sup>5</sup> The main chain modifications such as rubber-bound side products of vulcanization may also influence the physical properties. Since all the elements constituting the network structure viz., crosslink density, crosslink structure, and main chain modifications are influenced by the vulcanization temperature, there might be an optimum vulcanization temperature for a given rubber compound which gives the best compromise of physical properties for specific applications. In this study, filled compounds of natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) are vulcanized at different temperatures and the vulcanizate properties are compared.

## EXPERIMENTAL

## Preparation of Vulcanizates

The formulations employed for the study are shown in Tables I and II. The NR and SBR compounds were prepared on a laboratory mixing mill at about 50°C as per ASTM D 3184 (1973) and D 3186 (1973), respectively, and the BR

TABLE I  
Formulations of the Compounds—Conventional System

NR compound		SBR compound		BR compound	
NR <sup>a</sup>	100	SBR <sup>b</sup>	100	BR <sup>c</sup>	100
ZnO	5	ZnO	5	ZnO	5
Stearic acid	2	Stearic acid	2	Stearic acid	2
PBN <sup>d</sup>	1	PBN <sup>d</sup>	1	PBN <sup>d</sup>	1
HAF black (N 330)	40	HAF black (N 330)	40	HAF black (N 330)	40
Naphthenic oil	5	Naphthenic oil	5	Naphthenic oil	5
CBS <sup>e</sup>	0.6	CBS <sup>e</sup>	0.8	CBS <sup>e</sup>	0.7
TMTD <sup>f</sup>	0.1	TMTD <sup>f</sup>	0.3	TMTD <sup>f</sup>	0.15
Sulfur	2.5	Sulfur	2.2	Sulfur	2.4

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

<sup>b</sup>23.5% styrene; Mooney viscosity, ML (1 + 4) at 100°C, 49.2 (Synthetics and Chemicals Ltd., Bareilly).

<sup>c</sup>97% 1,4 (cis); Mooney viscosity, ML (1 + 4) at 100°C, 46.0 (Indian Petrochemicals Corporation Ltd.).

<sup>d</sup>Phenyl- $\beta$ -naphthylamine (Indian Explosives Ltd.).

<sup>e</sup>*N*-cyclohexyl-2-benzothiazyl sulfenamide (Indian Explosives Ltd.).

<sup>f</sup>Tetramethyl thiuram disulfide (Indian Explosives Ltd.).

TABLE II  
Formulations of the Compounds—EV System

NR compound		SBR compound		BR compound	
NR <sup>a</sup>	100	SBR <sup>b</sup>	100	BR <sup>c</sup>	100
ZnO	5	ZnO	5	ZnO	5
Stearic acid	2	Stearic acid	2	Stearic acid	2
PBN <sup>d</sup>	1	PBN <sup>d</sup>	1	PBN <sup>d</sup>	1
HAF black (N 330)	40	HAF black (N 330)	40	HAF black (N 330)	40
Naphthenic oil	5	Naphthenic oil	5	Naphthenic oil	5
CBS <sup>e</sup>	2.5	CBS <sup>e</sup>	2.5	CBS <sup>e</sup>	2.5
TMTD <sup>f</sup>	0.8	TMTD <sup>f</sup>	1.5	TMTD <sup>f</sup>	1.25
Sulfur	0.5	Sulfur	0.4	Sulfur	0.5

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

<sup>b</sup>23.5% styrene; Mooney viscosity, ML (1 + 4) at 100°C, 49.2 (Synthetics and Chemicals Ltd., Bareilly).

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<sup>d</sup>Phenyl- $\beta$ -naphthylamine (Indian Explosives Ltd.).

<sup>e</sup>*N*-cyclohexyl-2-benzothiazyl sulfenamide (Indian Explosives Ltd.).

<sup>f</sup>Tetramethyl thiuram disulfide (Indian Explosives Ltd.).

compounds were prepared on a laboratory intermix at about 80°C as per ASTM D 3189 (1973). The cure curves of the compounds were taken at 140°C, 150°C, 160°C, 170°C, and 180°C on a Goettfert elastograph model 67.85. The compounds were then vulcanized at 140°C, 150°C, 160°C, 170°C, and 180°C up to their respective optimum cure times (time for attaining 90% of the maximum torque) on an electrically heated laboratory hydraulic press.

### Determination of Crosslink Density<sup>6</sup>

Vulcanizate sample weighing 0.2–0.3 g was allowed to swell in excess of toluene containing 0.1% phenyl- $\beta$ -naphthylamine (PBN) at room temperature until equilibrium swelling. Then the sample was extracted for 2 h in pure toluene. The swollen sample was weighed, solvent removed by drying for 6 days at room temperature, and weighed again. The volume fraction of the rubber in the swollen vulcanizate ( $V_r$ ) was then calculated using the relation,<sup>7</sup>

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_o\rho_s^{-1}}$$

where  $T$  is the sample weight,  $D$  the deswollen weight,  $F$  the weight fraction of the insoluble components, and  $A_o$  the weight of the absorbed solvent corrected for swelling increment.  $\rho_r$  and  $\rho_s$  are the densities of the rubber and solvent, respectively. The value of  $V_r$  so obtained was then converted into  $V_{ro}$  (the value  $V_r$  would have had in the absence of the carbon black) by means of Kraus' equation,<sup>8</sup>

$$\frac{V_{ro}}{V_r} = 1 - \frac{m\phi}{1 - \phi}$$

where,

$m = V_{ro} - 1 + 3c(1 - V_{ro}^{1/3})$ ,  $\phi$  = volume fraction of the carbon black in the rubber mix, and  $c$  = parameter for carbon black (in the case of N 330,  $c = 1.20$ ).  $V_{ro}$  was then substituted in place of  $V_r$  in the Flory-Rehner equation,<sup>9,10</sup>

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

where  $\rho_r$  is the density of the rubber matrix  $V_s$ , the molar volume of the solvent, and  $\chi$  is an interaction constant characteristic of both rubber and swelling liquid. The crosslink density ( $1/2M_c$ ) was then determined.

### Determination of Physical Properties

The tensile properties of the vulcanizates were determined according to ASTM D 412 (1980) using dumbbell specimens on a Zwick universal testing machine model 1445 at 25°C using a crosshead speed of 500 mm/min. The hardness was determined as per ASTM D 2240 (1981) and expressed in shore A units. The tear resistance of the vulcanizates was determined as per ASTM

D 624 (1981) using unnicked 90° angle test piece at 25°C at a crosshead speed of 500 mm/min. Aging resistance of the vulcanizates was determined by keeping them in an air oven at 100°C for 48 h and then measuring the retention in the physical properties. The crosslink density of the vulcanizates was also determined after aging.

## RESULTS AND DISCUSSION

### Conventional System

The cure characteristics of the compounds at 140°C, 150°C, 160°C, 170°C, and 180°C taken from the cure curves are shown in Table III. The curing quickens with increased vulcanization temperature as seen from the sharp reduction in the cure times. The scorch safety also decreases (as indicated by the decrease in the scorch times calculated as the time required for a 2 unit (0.02 Nm) rise over the minimum torque) with increased vulcanization temperature as expected. The maximum torque, a measure of the crosslink density, decreases with increased vulcanization temperature in all three cases. This indicates that the crosslink density decreases with increased vulcanization temperature. The molecular changes resulting in a reduction in overall viscosity of the system may be another reason for the decrease in the maximum torque.<sup>11</sup>

The variation of the crosslink density of the vulcanizates with vulcanization temperature is also shown in Table III. The total crosslink density is found to decrease with increase in vulcanization temperature for NR, SBR, and BR. This indicates that the network structures formed at various vulcanization temperatures are different, with possible changes occurring in the crosslink structure and main chain modifications also. A significant change in the crosslink structure might be an increase in the percentage of polysulfidic crosslinks which could lead to an overall reduction in the crosslink density. This suggests that the desulfuration of polysulfidic eventually crosslinks to corresponding monosulfidic linkages with the recirculation of the removed sulfur into the crosslinking pathways occurs more often at lower curing temperatures, probably due to the longer cure times.<sup>12</sup> The crosslink density of the NR vulcanizates is low compared to that of SBR and BR. This shows that the network structure of the NR vulcanizates is significantly different from that of SBR and BR. Among the three rubbers, NR probably has the maximum percentage of polysulfidic crosslinks, which may be a prominent reason for the comparatively low crosslink densities.

In the case of SBR and BR, the crosslink density of all the vulcanizates increases with thermal aging, while for NR there is a reduction in the crosslink density for most of the vulcanizates, particularly for those cured at lower temperatures. This indicates that SBR and BR vulcanizates have more stable network structures than NR, and shortening of the polysulfidic crosslinks seems to be the most important network change occurring in SBR and BR while for NR main chain modifications are also active during aging.

Variations of tensile strength and elongation at break of the NR, SBR, and BR vulcanizates with curing temperature is shown in Figures 1, 2, and 3, respectively. Tensile strength increases initially, reaches a maximum, and then

TABLE III  
 Characterization of Vulcanizates—Conventional System

Rubber Cure tempera- ture (°C)	NR				SBR				BR						
	140	150	160	170	180	140	150	160	170	180	140	150	160	170	180
Optimum cure time (min)	10.20	5.25	2.77	1.74	1.15	17.00	9.15	5.25	3.18	1.98	13.50	6.60	4.20	2.25	1.65
Scorch time (min)	4.80	2.25	1.50	0.96	0.66	6.00	2.85	2.10	1.20	0.78	3.3	2.1	1.35	1.2	0.75
Maximum torque (Nm)	0.614	0.593	0.564	0.550	0.543	0.986	0.979	0.961	0.943	0.921	1.20	1.14	1.01	0.94	0.87
Crosslink den- sity (mmol/ kg. RH) <sup>a</sup>	58.60	56.75	53.70	40.03	30.70	105.79	99.10	93.20	87.90	76.50	105.72	105.22	94.92	85.36	70.26
Tear strength (N/mm)	86.7	90.0	82.7	71.7	58.0	44.6	46.5	48.1	45.9	44.1	38.0	40.0	40.0	38.5	36.0
Hardness (Shore A)	57.5	57.0	56.5	55.0	52.0	64.5	64.4	64.0	62.5	61.0	68.44	68.19	66.81	64.62	62.43
After aging															
Crosslink den- sity (mmol/ kg. RH) <sup>a</sup>	43.20	43.30	40.54	39.00	31.0	129.4	124.9	121.5	119.3	106.8	128.38	127.15	126.37	123.38	105.96
Hardness (Shore A)	54.5	54.0	53.0	51.5	48.5	70.0	70.5	69.0	68.0	66.0	72.18	72.25	70.56	70.13	69.13

<sup>a</sup> Millimole/kg of rubber hydrocarbon.

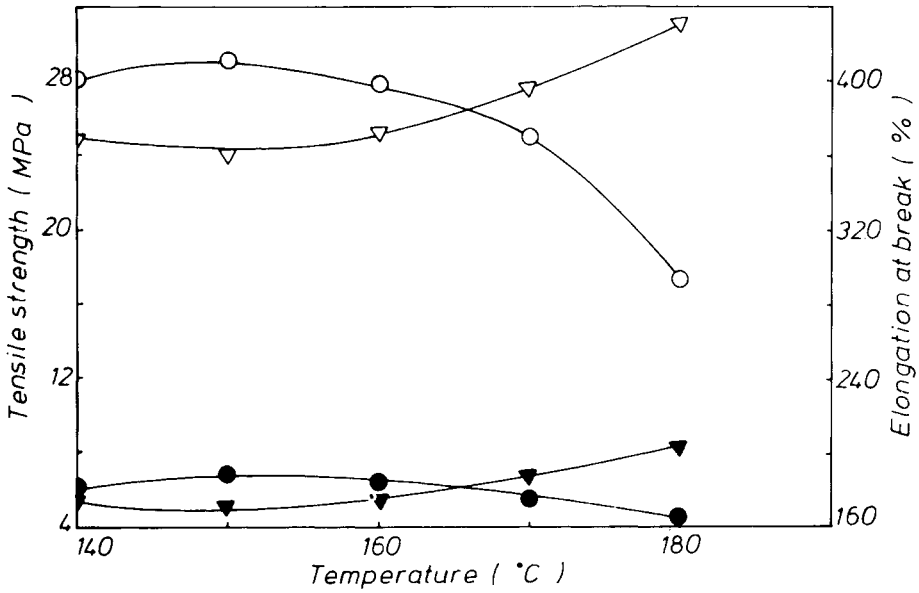


Fig. 1. Variation of tensile strength (○) and elongation at break (▽) of NR (conventional system) with vulcanization temperature: (○,▽) before aging, (●,▼) after aging.

starts decreasing in all three cases. This shows that for a given rubber compound there is an optimum vulcanization temperature, which produces a network structure resulting in maximum tensile strength. In the case of the NR compound, this temperature is about 150°C, for SBR about 160°C, and BR about 155°C. A larger fraction of polysulfidic crosslinks at these tempera-

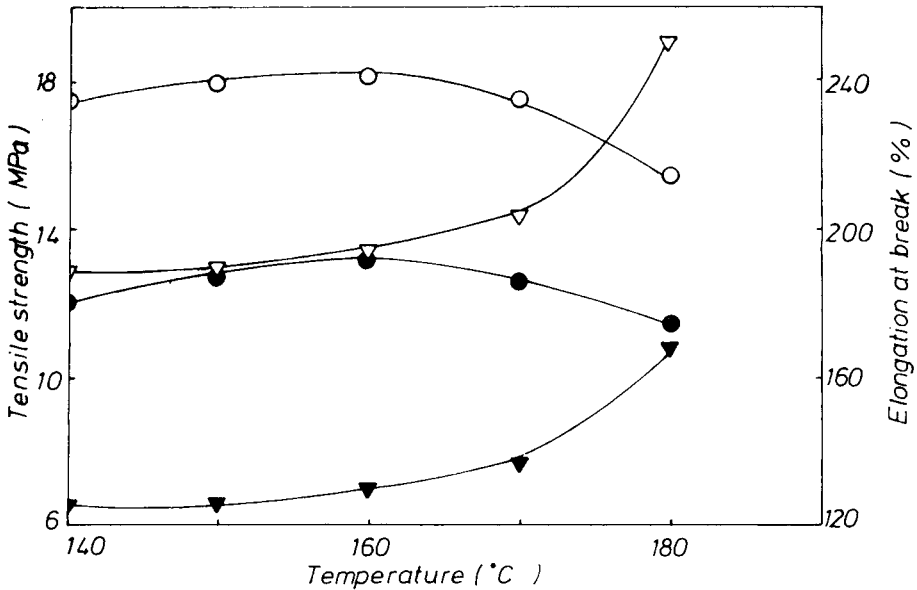


Fig. 2. Variation of tensile strength (○) and elongation at break (▽) of SBR (conventional system) with vulcanization temperature: (○,▽) before aging, (●,▼) after aging.

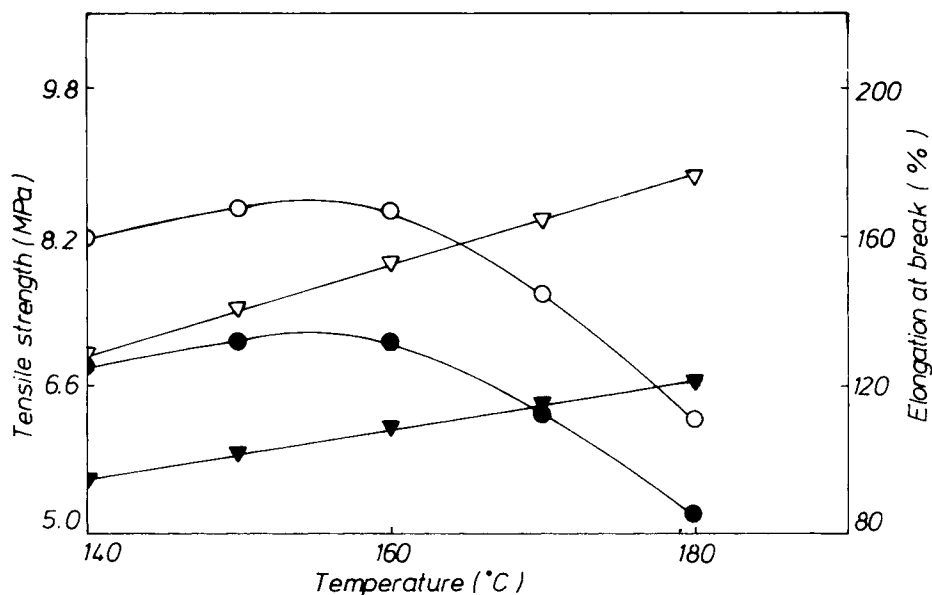


Fig. 3. Variation of tensile strength (○) and elongation at break (▽) of BR (conventional system) with vulcanization temperature: (○, ▽) before aging; (●, ▼) after aging.

tures than at lower temperatures,<sup>13</sup> coupled with other network changes cause this maxima in strength.

The retention in tensile strength with aging remains more or less constant with the curing temperature. Elongation at break increases for NR, SBR, and BR when the curing temperature is raised. This is obviously due to the reduction in the crosslink density and increase in the percentage of polysulfidic crosslinks with the increase in the curing temperature. The retention in elongation at break decreases with increase in curing temperature. This may be due to the enhanced increase in crosslink density on aging with increase in vulcanization temperature. The tear strength of rubber vulcanizates is a complex function of the elastomer used, crosslink density, filler content, plasticizer content, etc.<sup>14</sup> Variation of tear strength with vulcanization temperature shows close similarities with tensile strength. The maximum tear strength for NR is observed at 150°C, for SBR at 160°C, and BR at 155°C as in the case of the tensile strength.

Variations of hardness with vulcanization temperature corresponds to the variation of crosslink density as expected.<sup>3</sup>

### EV System

The cure characteristics of the compounds and the crosslink density and the physical properties of the vulcanizates are shown in Table IV. The optimum cure time, scorch time, and maximum torque decrease with increase in the vulcanization temperature as expected. The variation of crosslink density with curing temperature is similar to that observed in the case of conventional systems; crosslink density decreases with increase in curing temperature.

TABLE IV  
Characterization of Vulcanizates—EV System

Rubber Cure tempera- ture (°C)	NR			SBR			BR						
	140	150	160	140	150	160	140	150	160	170	180		
Optimum cure time (min)	13.00	6.30	3.30	22.50	11.85	6.39	3.54	2.40	17.1	7.8	4.35	3.75	1.95
Scorch time (min)	4.20	2.10	1.35	6.00	3.85	2.03	1.20	0.72	3.3	2.1	1.35	0.9	0.75
Maximum Torque (Nm)	0.705	0.689	0.674	0.868	0.857	0.849	0.821	0.814	1.13	1.09	1.08	1.06	0.89
Crosslink den- sity (mmol/ kg. RH) <sup>a</sup>	43.38	42.84	42.10	77.27	74.77	70.88	68.16	55.49	91.79	89.06	86.99	81.06	71.83
Tear strength (N/mm)	67.2	70.3	67.1	38.5	41.6	43.8	41.2	40.0	35.0	36.0	36.0	34.0	33.0
Hardness (Shore A)	58.5	58.0	57.0	60.0	61.0	60.5	59.0	56.5	66.56	67.25	65.18	64.55	62.56
<i>After aging</i> Crosslink den- sity (mmol/ kg. RH) <sup>a</sup>	49.90	49.51	48.15	91.33	85.02	79.28	77.96	64.58	113.31	110.87	110.35	102.75	91.69
Hardness (Shore A)	59.0	59.0	58.5	64.0	63.5	62.5	61.0	59.0	72.87	73.06	72.21	70.75	67.50

<sup>a</sup> Millimole/kg of rubber hydrocarbon.



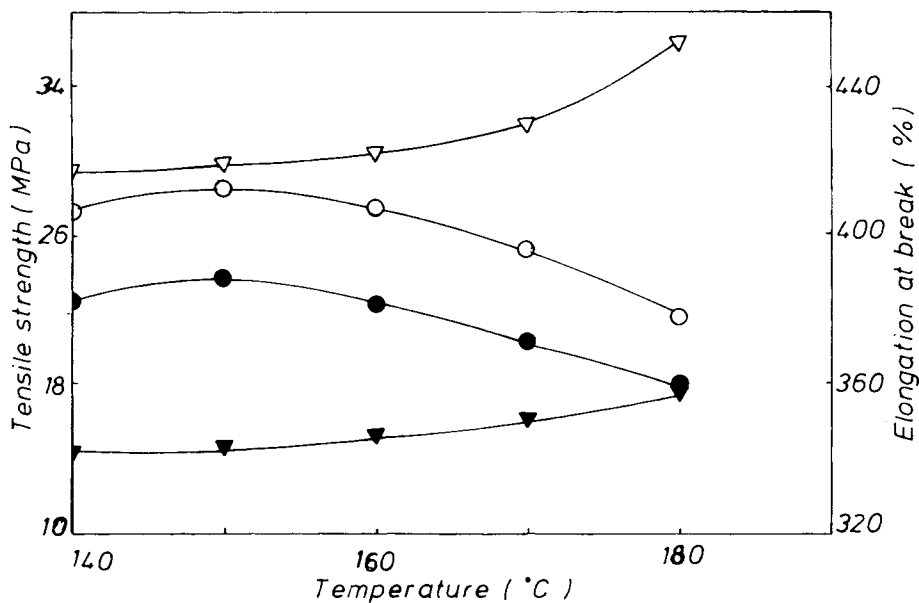


Fig. 4. Variation of tensile strength (○) and elongation at break (▽) of NR (EV system) with vulcanization temperature: (○, ▽) before aging, (●, ▼) after aging.

However the variation in crosslink density is less in this case than in the previous case. This might be due to the lower percentage of polysulfidic crosslinks in all the cases. The crosslink density increases with aging for all the vulcanizates including that of NR. This shows that vulcanizates have more stable network structure in this case and that shortening of the polysul-

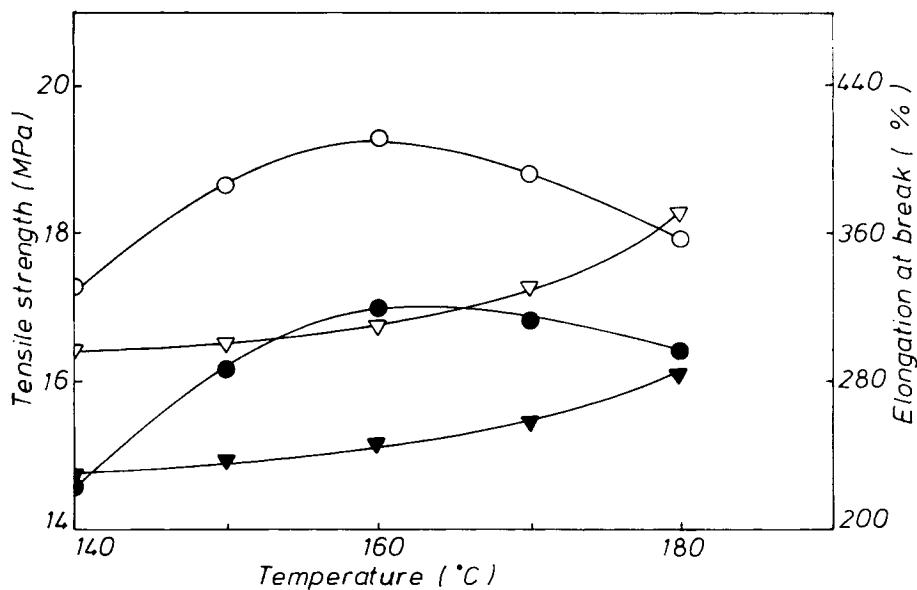


Fig. 5. Variation of tensile strength (○) and elongation at break (▽) of SBR (EV system) with vulcanization temperature: (○, ▽) before aging; (●, ▼) after aging.

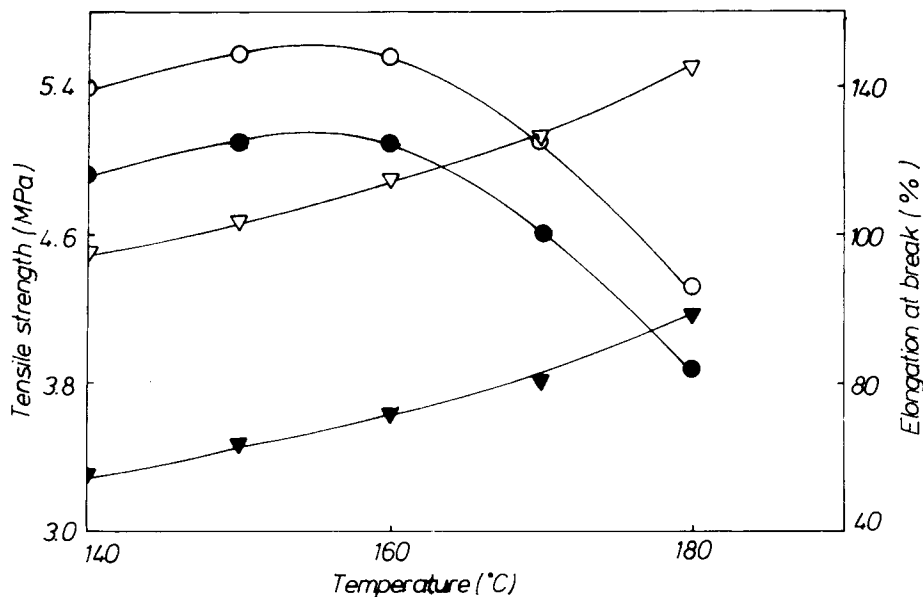


Fig. 6. Variation of tensile strength (○) and elongation at break (▽) of BR (EV system) with vulcanization temperature: (○, ▽) before aging; (●, ▼) after aging.

fidic crosslinks with additional crosslinking is probably the significant change in this case during aging.

The variation of tensile strength and elongation at break with curing temperature of NR, SBR, and BR (Figs. 4, 5, and 6) is similar to their conventional vulcanizates. The maximum tensile strength for NR is observed at 150°C, for SBR at 160°C, and BR at 155°C as before. However, the tensile strength and elongation at break are generally less in this case probably due to the decrease in the concentration of polysulfidic crosslinks. The retention in these properties with aging is much superior compared to that of the conventional vulcanizates as expected. The maximum values of tear strength for NR, SBR, and BR also occur at 150°C, 160°C, and 155°C, respectively. The hardness values again bear a direct relationship with the crosslink density.

## CONCLUSION

For a given rubber compound, the curing temperature has a profound influence on the network structure and hence on the mechanical properties of the vulcanizate. Hence the curing temperature for a particular product could be fixed based on the properties required of it. Since the aging resistance of the vulcanizates cured at different temperatures is more or less the same, the improved properties acquired by choosing a particular curing temperature will—at least in part—survive aging.

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