Effect of vulcanization temperature and vulcanization systems on the structure and properties of natural rubber vulcanizates

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The effect of vulcanization temperature (150°–180°C) on the structure and technical properties of gum natural rubber vulcanizates with four different 2-(morpholinodithio)-benzothiazole: sulphur ratios (A, 0.6:2.4; B, 1.5:1.5; C, 2.4:0.6; D, 3.0:0.0) at the respective optimum cure times has been determined. The influence of cure temperature on (a) the chemical crosslink density; (b) the distribution of crosslink types; (c) the extent of sulphidic main chain modifications and (d) the zinc sulphide formation was investigated. Results show that elevated cure temperatures produce a network with lower crosslink density, in particular a lower polysulphidic crosslink density. The formation of intramolecular sulphidic groups and zinc sulphide increase with increasing cure temperatures. The possibility of chain scission during vulcanization, as examined by a quantitative analysis of the sol–gel data, was found to be negligible. The network results have been correlated with the technical properties.

INTRODUCTION

In recent years study of high temperature vulcanization has gained importance in order to reduce the cure cycle times[1]. Chernyak *et al.*[2] have studied the effect of different accelerators on the vulcanizate structure of natural rubber (NR) mixes in conventional sulphur vulcanization systems. Chavchich *et al.*[3] have recently studied the combination of sulphur, sulphur donor (i.e. dithiodimorpholine) and sulphenamide accelerator with respect to the vulcanizate structure in the high temperature vulcanization of NR–cis-1,4-polybutadiene blend. Shapkim and coworkers[4] found that vulcanizing systems containing *N,N'*-dithiodimorpholine 1.5, sulphenamide 1.5 and *N,N'*-tetrathiodimorpholine 0.5 weight parts in 100 weight parts polyisoprene rubber can be used effectively at a curing temperature of 180°C. Loo and coworkers[5–8] have studied extensively the correlation between vulcanizate structure and properties of vulcanizates in the conventional and efficient vulcanization (*EV*) systems accelerated by *N*-cyclohexyl-2-benzothiazyl sulphenamide (CBS) in NR mixes. It was found that a mix with 3.5 phr CBS:1.5 phr sulphur was more suitable for high temperature vulcanization than the conventional cure system (0.5 phr CBS:2.5 phr sulphur) as better technological properties were obtained.

2-(Morphholinodithio)-benzothiazole (MDB) has the remarkable ability of being both a vulcanizing agent for polydiene rubbers when used without elemental sulphur and a delayed action sulphenamide type accelerator of sulphur vulcanization[9]. By varying the ratio of sulphur to MDB, vulcanization systems grading from conventional to *EV* can be obtained. In the present paper, we have studied the effect of vulcanization temperature (150° to 180°C) in such graded systems from 2.4 phr sulphur:0.6 phr MDB to 0 phr sulphur: 3 phr MDB, on the structure and technological properties of unfilled natural rubber vulcanizates.

EXPERIMENTAL

Vulcanizate preparation

Table 1 gives the formulation of the four rubber mixes studied and *Table 2* gives their curing characteristics at 150°, 160°, 170°, and 180°C, obtained from the Bayer vulkameter. The mixes were prepared on a laboratory mill. The $\overline{M}_n$ value of the rubber hydrocarbon component in the mix was determined from the limiting viscosity number, $[\eta]_{\text{toluene}}$ (dl/g) at 25°C by means of the relationships[10]:

$$[\eta]_{\text{toluene}} = 1.076[\eta]_{\text{benzene}} - 0.15$$

$$\text{and } [\eta]_{\text{benzene}} = 2.29 \times 10^{-7}\overline{M}_n^{\,1.33}$$

The $\overline{M}_n$ values of the rubber hydrocarbon in all mixes was in the range of 1.4×10^5 to 1.5×10^5. Vulcanization was carried out in an electrically heated press for optimum cure

Table 1 Composition of the mixes

Parts weight	A	B	C	D
Natural rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
MDB	0.6	1.5	2.4	3.0
Sulphur	2.4	1.5	0.6	0.0

Table 2 Curing characteristics of different mixes

	Curing temperature (°C)	A	B	C	D
Scorch time (t_{20} min)	150	12.0	13.6	13.6	25.2
	160	7.2	8.0	8.8	16.6
	170	4.0	4.2	5.0	10.0
	180	2.6	3.0	3.3	6.0
Optimum cure time (t_{90} min)	150	23.0	21.0	28.0	60.0
	160	14.0	12.0	14.0	32.0
	170	6.0	6.0	8.0	17.0
	180	4.0	4.0	5.0	10.0
Reversion time (min) (time required to reach 98% of maximum cure after the maximum has been attained)	150	47.0	54.0	83.0	128.0
	160	24.0	24.0	32.0	79.0
	170	12.0	11.0	22.5	29.5
	180	7.0	7.5	14.5	15.0

times of different mixes obtained at different cure temperatures (*Table 2*). Mouldings were cooled quickly in water at the end of the curing cycle.

Determination of chemical crosslink density and crosslink type

The density of chemical crosslinks was estimated from the value of the elastic constant C_1 using the Mullins relationship[11] which accounts for the contribution of chain ends and physical entanglements in the natural rubber vulcanizates:

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

where ρ is the vulcanizate density, R is molar gas constant, T is the absolute temperature, $\bar{M}_n$ is the initial molecular weight of rubber hydrocarbon in the mix, $(2M_{c,chem})^{-1}$ is the density of chemical crosslinks and is reported as number of g mol/g rubber hydrocarbons. C_1, the elastic constant pertinent to the rubber hydrocarbon in the vulcanizate was caculated from the following relation[12,16]:

$$-[\ln(1 - V_r) + V_r + \chi V_r{}^2] = 2C_1V_s\left(V_r{}^{1/3} - \frac{V_r}{2}\right)\Bigg/RT$$

where V_r, V_s, and χ are the volume fraction of rubber network in the swollen gel, molar volume of the swelling liquid and the Flory–Huggins solvent–rubber interaction parameter, respectively. The value of χ changes with changes in recipes. As the recipe changes, V_r changes. χ can be correlated with V_r according to the following relation[13]:

$$\chi = \chi_0 + \beta V_r$$

where χ equals χ_0 (= 0.44) when V_r is very small and β is an empirical constant equal to 0.18 for the NR–benzene system. The proportions of mono-, di-, and polysulphide crosslinks were estimated from the determination of chemical crosslink densities before and after treatment with thiol–amine chemical probes[14,15].

The crosslinking efficiencies, denoted by E and E' were calculated as the number of atoms of sulphur combined in the vulcanizate network per chemical crosslink before and after treatment with triphenylphosphine[16]. The E value is interpreted as a measure of overall structural complexity of a sulphur-vulcanized network, while E' is a direct measure of sulphur combined in the main chain modifications such as the cyclic sulphidic groups and pendant sulphidic groups.

The total sulphur was determined by the combustion of the extracted vulcanizates (about 0.2 g) in oxygen. The sulphur dioxide produced was absorbed by hydrogen peroxide, and the resultant sulphate ions were quantitatively titrated[16].

Sulphide sulphur was determined iodometrically from the

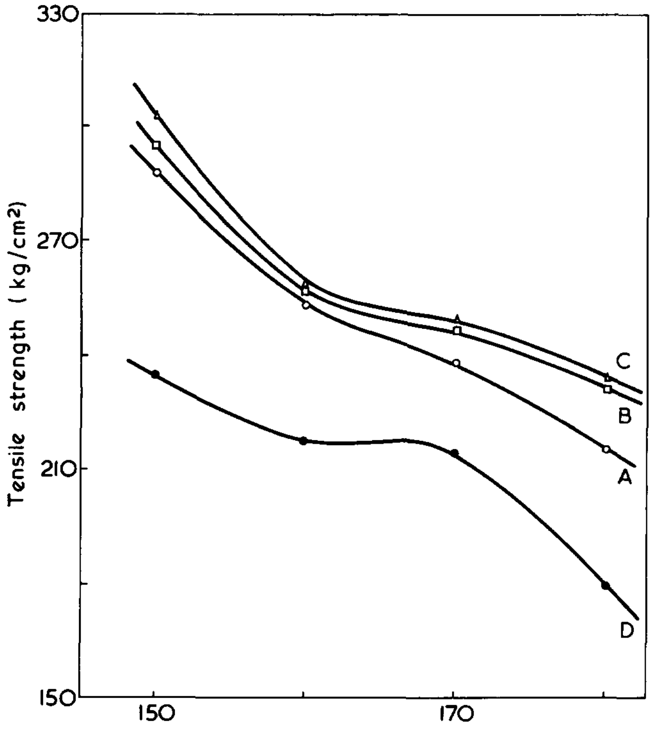

Figure 1 Plot of tensile strength against cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0

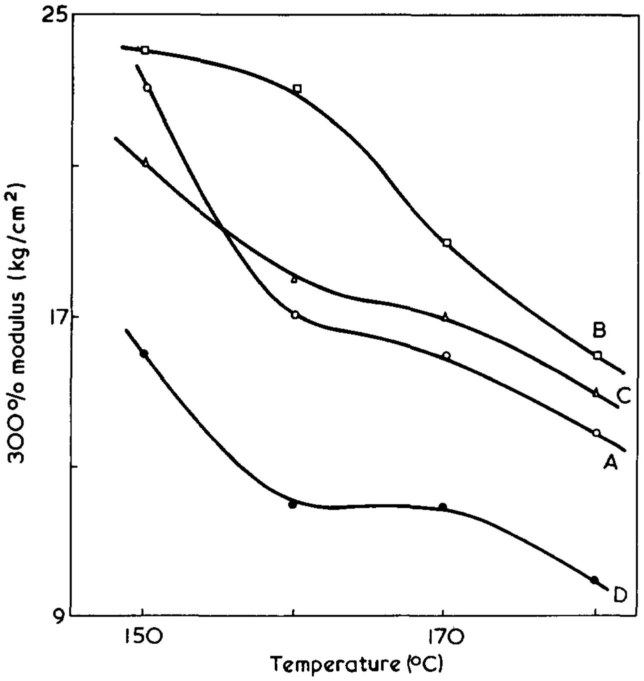

Figure 2 Plot of modulus (300%) *versus* cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0

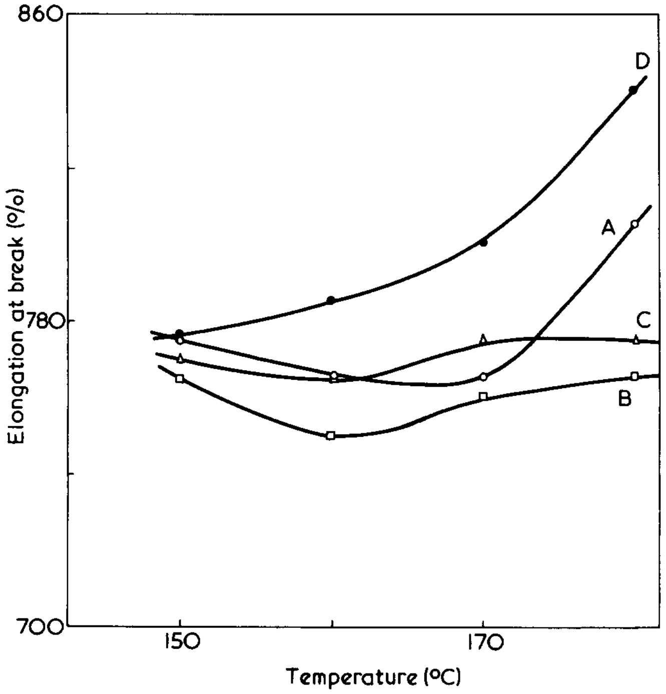

Figure 3 Plot of elongation at break against cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0

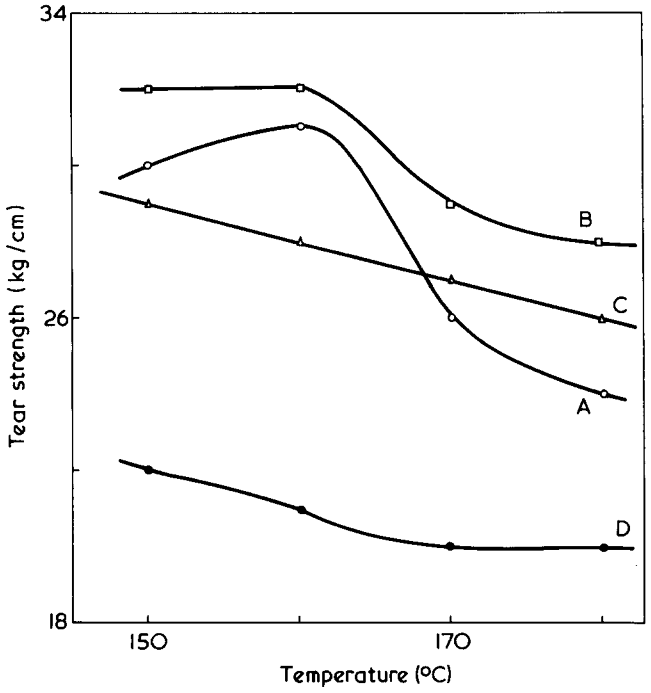

Figure 4 Plot of tear strength *versus* cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0

formation of cadmium sulphide[17]. *F* values were defined and calculated as the number of g ions of sulphide sulphur present in the network per chemical crosslink.

Determination of the sol and gel fractions of the vulcanizates was carried out by extracting with hot acetone in the dark for 3 days, and drying to constant weight *in vacuo* at room temperature. Weighed samples of extracted vulcanizates (about 1 g) were continuously extracted with cold benzene in the dark, for 8–10 days, the benzene being renewed three times during this period. After benzene extraction, samples were dried to constant weight *in vacuo*. The sol fraction (S) was then estimated from the loss in weight during benzene extraction. Sol determinations were made in duplicate.

The gel fraction (q, fraction of sites at which crosslinking has occurred) was calculated from $(2M_{c,chem})^{-1}$ at each point. These sol–gel data were analysed using the Charlesby and Pinner equation[18]:

$$S + S^{1/2} = pq^{-1} + (q\bar{y}_n)^{-1}$$

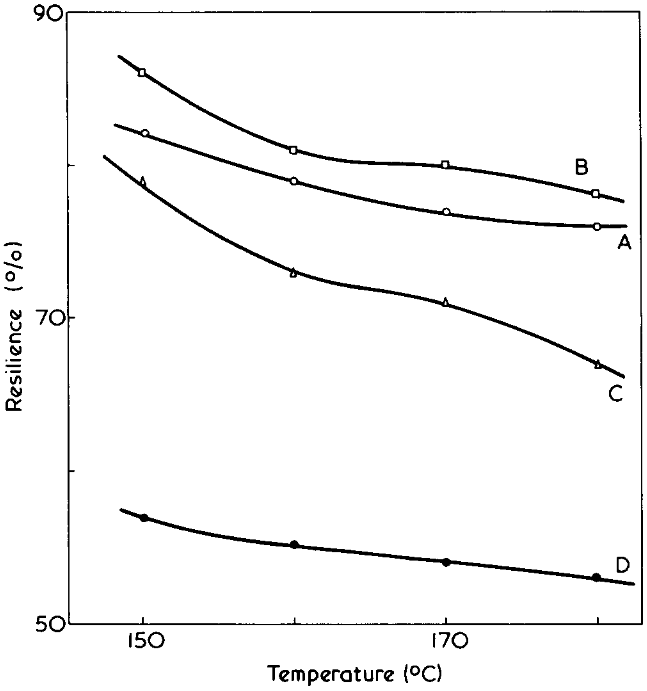

Figure 5 Plot of resilience against cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0

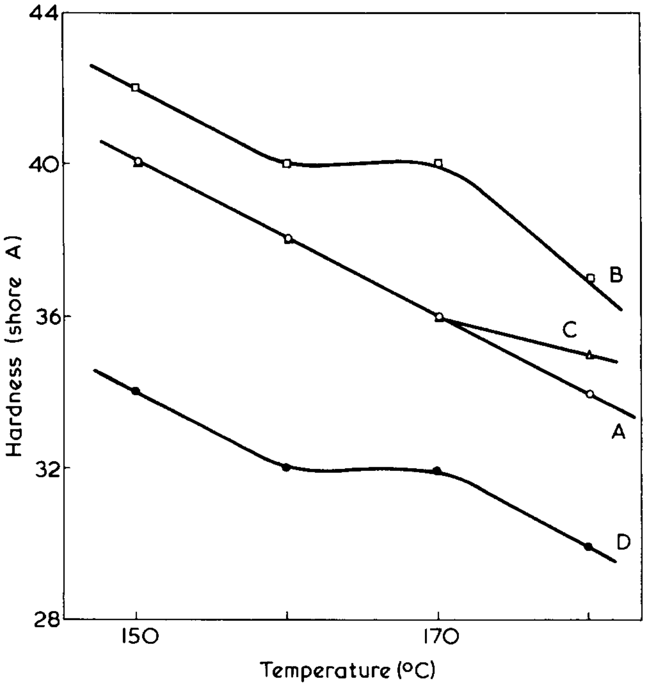

Figure 6 Plot of shore hardness *versus* cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0

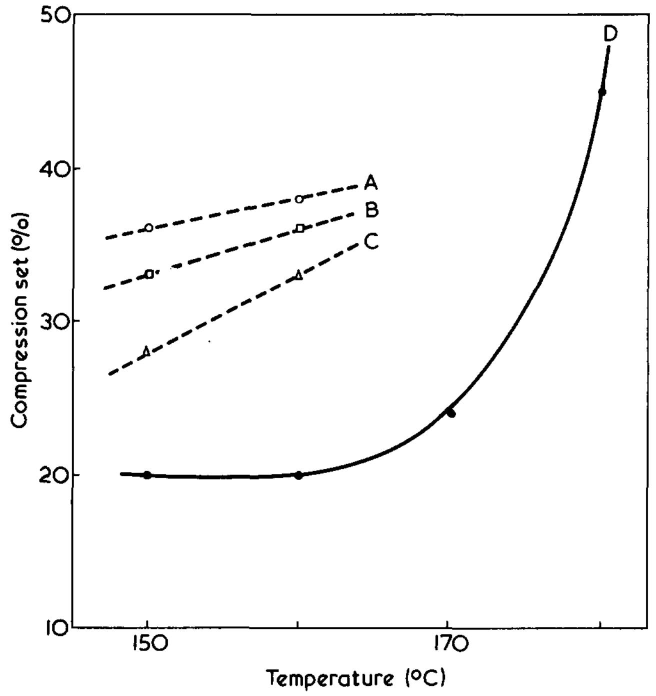

Figure 7 Plot of compression set against cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0

where S is the sol fraction, p is the fraction of sites at which random scission has occurred, and $\bar{y}_n$ is the number-average chain length of an uncured polymer having a random chain length distribution.

Vulcanizate properties

Tensile strength, modulus and elongation at break were determined in a Zwick tensile testing machine[19], and the tear resistance was found[20]. Shore A hardness was determined[21]. Impact resilience was obtained at 35°C using a Dunlop Tripsometer[22]. Compression set was determined[23], and a De Mattia machine was used to determine flex cracking at 70° ± 1°C[24]. In the case of crack growth test an initial cut of 0.08 in. was made using a Satra piercing tool. Ageing study was carried out in an air oven (Model No FC712, Blue M. Electric Co.) at 100° ± 0.5°C.

RESULTS AND DISCUSSION

As expected in all mixes the scorch time, optimum cure time and reversion time decrease with increase in vulcanization temperature (*Table 2*). Mix C and mix D were found to exhibit superior reversion resistance to mix A and mix B. This is attributed to the fact that vulcanizates of mix C and mix D, as discussed below, contain higher proportions of disulphidic and monosulphidic crosslinks than polysulphidic crosslinks.

Results of the technological properties are shown in *Figures 1* to *7*. Tensile, tear, modulus (300%), hardness and

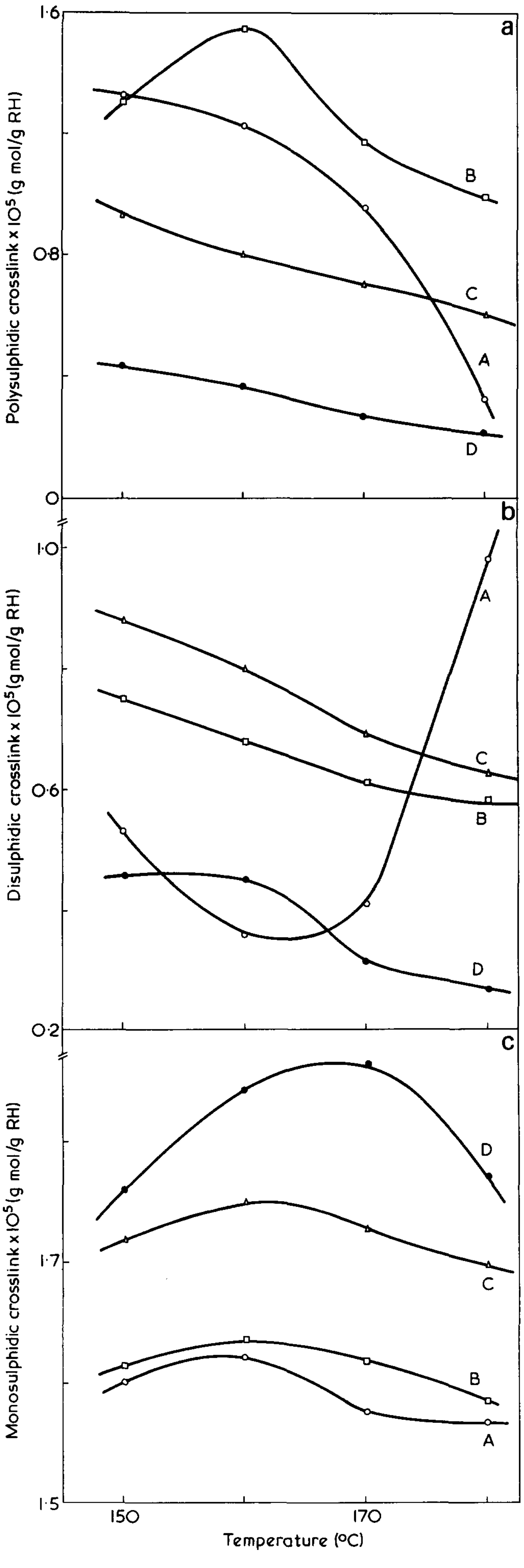

Figure 8 (a) Plot of polysulphidic crosslink *versus* cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0. (b) Plot of disulphidic crosslink against cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0. (c) Plot of monosulphidic crosslink *versus* cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0

resilience properties of the vulcanizates decrease as the cure temperature increases in all mixes. The deterioration in properties at high cure temperature is attributed to lower state of crosslinking and changes in the vulcanizate structure. At a particular temperature the properties generally attain a maximum for the mix B, followed by mix C, mix A and mix D.

The behaviour of technological properties could be understood from the crosslink densities and type of crosslinks (*Table 3* and *Figures 8a, 8b* and *8c*). Mix B attained the maximum and mix D the minimum crosslink densities at all cure temperatures. Polysulphidic crosslinks in general decrease with increase in cure temperature. Disulphidic crosslinks in mix A decrease with increase in cure temperature, reach a minimum at 160°C and then again start increasing at higher temperature. For other mixes, disulphidic crosslinks decrease with increase in cure temperature. Monosulphidic crosslinks in all mixes increase with cure temperature, reach a maximum around 160°–170°C and then decrease at 180°C.

As the sulphur to accelerator ratios decrease in the mixes, both E and E' values decrease at all cure temperatures. This observation indicates that the sulphur is more efficiently used for forming the crosslinks at low S: MDB ratios. It was found that the increase in vulcanization temperature beyond 160°C tends to increase both E and E'. This observation indicates less efficient use of sulphur in the formation of crosslinks and increased modifications of the main chain at high curing temperatures.

Mix D and mix C have very low F values at all curing temperatures while mix A and mix B showed F values around unity at 150° and 160°C. At higher curing temperatures F values increase, suggesting that more zinc sulphide was produced at the expense of crosslink formation. It is apparent that the lower level of some technological properties in mix D is due to the lower level of chemical crosslinks in the structure, in particular a lower number of polysulphidic crosslinks. The lower level of properties at curing temperature of 170° and 180°C is possibly due to main chain modification which inhibits strain-induced crystallization[6].

Flex cracking resistance showed a peculiar behaviour (*Figures 9a* and *9b*). At 150°C, flex resistance decreases in the order, A > B > C > D. The flex resistance decreases with increase in cure temperature, but beyond 170°C the

Table 3 Chemical characterization of vulcanizate networks

Curing temperature (°C)	Sample	$[2M_{c,chem}]^{-1}$ X 10^5 (g mol/g RH)	Network combined sulphur X 10^4 (g atoms/g RH)		Sulphur efficiencies (atoms/chemical crosslink)		$[S_c]$ (%) removed by Ph_3P treatment	$[S^{2-}]$sulphide sulphur X 10^4 (g ion/g RH)	F (sulphide ion/chemical crosslink)
			$[S_c]$ before Ph_3P treatment	$[S'_c]$ after PH_3P treatment	E, before Ph_3P treatment	E', after Ph_3P treatment			
150	A	3.45	5.15	2.68	14.9	7.8	48	0.46	1.33
	B	3.62	4.21	2.28	11.6	6.3	46	0.50	1.38
	C	3.53	3.50	2.33	9.9	6.6	33	0.05	0.14
	D	2.65	2.06	1.32	7.8	5.0	36	0.00	0.00
160	A	3.21	4.87	2.70	15.2	8.4	44	0.34	1.05
	B	3.86	3.78	2.70	9.8	7.0	28	0.41	1.06
	C	3.35	2.87	2.48	8.6	7.4	14	0.11	0.32
	D	2.65	2.12	1.38	8.0	5.2	35	0.00	0.00
170	A	2.94	4.71	2.67	16.0	9.1	43	0.71	2.41
	B	3.40	3.53	2.62	10.4	7.7	26	0.56	1.64
	C	3.11	3.59	2.52	11.5	8.3	30	0.05	0.15
	D	2.45	2.05	1.49	8.4	6.1	27	0.00	0.00
180	A	2.88	4.93	2.99	17.1	10.4	39	0.69	2.39
	B	3.15	3.87	2.87	12.3	9.1	26	0.56	1.77
	C	2.93	3.75	2.69	12.8	9.2	28	0.08	0.27
	D	2.27	2.15	1.71	9.4	7.5	20	0.00	0.00

Table 4 Retention of physical properties after 2 days ageing at 100°C

Curing temperature (°C)	Sample	Tensile strength (% retained)	Tear strength (% retained)	300% Modulus (% retained)	Elongation at break (% retained)	Hardness change
150	A	38	47	91	75	–8
	B	44	75	160	65	+1
	C	62	83	128	73	±0
	D	55	86	81	90	–4
160	A	15	39	–	38	–9
	B	20	50	–	39	–4
	C	51	68	111	75	–3
	D	46	65	92	88	–6
170	A	13	38	–	33	–9
	B	17	41	–	36	–5
	C	48	59	94	71	–3
	D	37	60	60	83	–7
180	A	12	25	–	31	–7
	B	15	38	–	36	–4
	C	42	54	106	59	–3
	D	28	52	90	79	–6

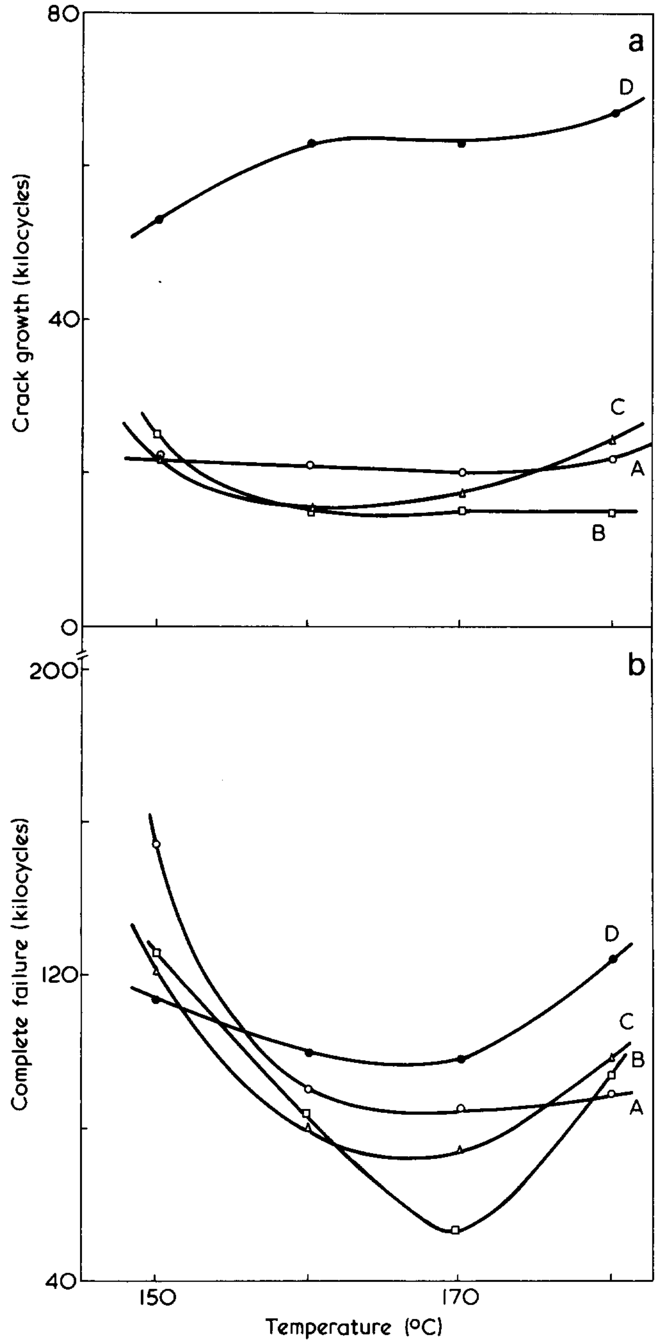

Figure 9 (a) Plot of crack growth against cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0. (b) Plot of complete failure *versus* cure temperature for different mixes: A, S:MDB = 2.4:0.6; B, S:MDB = 1.5:1.5; C, S:MDB = 0.6:2.4; D, S:MDB = 0:3.0

flex resistance increases and at 180°C the order is reversed. It is believed that improved fatigue life in high temperature curing is due to the stress relaxation caused by the lower state of crosslinking. This observation is similar to that observed by other workers[3,25–27]. At all curing temperatures, formulation D showed the best crack growth resistance. It has been postulated that shorter sulphur bridges in the crosslinks improve crack growth resistance[28].

Compression set data (*Figure 7*) indicates that as we move from mix A to mix D, compression set decreases. This is expected because of the less number of sulphur atoms in the crosslinks in mix D. The higher compression set observed at 180°C is due to the lower degree of crosslinking.

Figure 10 is the Charlesby–Pinner plot of the sol–gel data of mix B. A linear fit to all the data proves that there is negligible dependence of the ratio of scission/crosslinking on cure temperature in the range 150°–180°C. The linear equation derived from the application of the least squares principle is:

$$S + S^{1/2} = -0.133 + 1.001 \times 10^{-3} q^{-1}$$

A value of pq^{-1} of −0.133, which is not very different from zero, suggests that there is no chain scission during vulcanization at 150°–180°C. As a check on the accuracy of the plot (*Figure 10*), the value of $\bar{M}_n$, computed from the slope of the line is 1.35×10^5 which is very close to the $\bar{M}_n$ value of 1.45×10^5 obtained using the solution viscosity method.

Percent retention of properties after 2 days ageing at 100°C is shown in *Table 4*. It is evident that ageing resistance follow the order, C > D > B > A. This order is quite consistent with the presumed network structure of the vulcanizate. Vulcanizates of mix C and mix D contain higher proportions of disulphidic and monosulphidic crosslinks than they do of polysulphidic crosslinks. Moreover, the number of sulphur atoms in the pendant groups of mix C and mix D is likely to be less as compared to mix A and mix B (*Table 3*). Parks, Parker and Chapman have shown from oxygen absorption measurements that vulcanizates containing lower amount of sulphur in the original pendant groups resulted in superior ageing[29].

It appears from the evidence so far available that a satisfactory balance between technological properties, reversion resistance of the vulcanizates can be obtained by using mix C (that is, 0.6 phr sulphur:2.4 phr MDB).

Studies on kinetics and mechanism of vulcanization of different mixes under high cure temperatures are in progress in this laboratory.

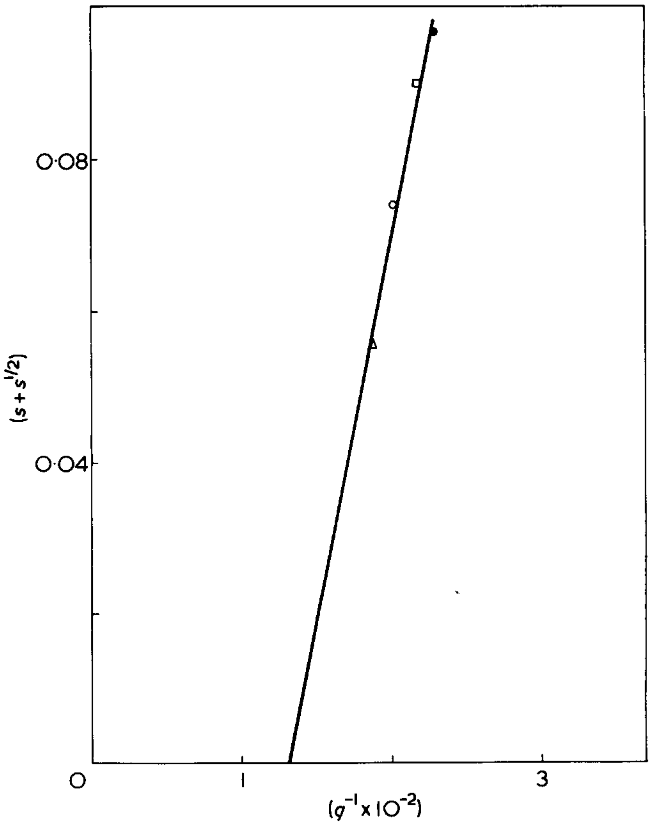

Figure 10 Plot of $(S + S^{1/2})$ *versus* (q^{-1}) for mix B at 150°–180°C: ○ 150°C; △, 160°C; □, 170°C; ●, 180°C

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