Structural Characterization of Vulcanizates. Part VI. The 2-Mercaptobenzothiazole-Accelerated Natural Rubber–Sulfur System

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Synopsis

The crosslinking efficiency of sulfur in the vulcanization of natural rubber in the presence of 2-mercaptobenzothiazole, zinc oxide, and lauric acid has been determined as a function of cure time, cure temperature, and lauric acid concentration. With a low concentration of lauric acid structurally complex networks are formed, which contain 11–19 combined sulfur atoms per chemical crosslink present. The complexity increases with time of vulcanization. With a high lauric acid concentration much simpler networks are formed, which become progressively more simple as reaction proceeds (6 network-combined sulfur atoms per chemical crosslink, decreasing to 2.4 with time). Increasing the cure temperature from 100 to 140°C. reduces the efficiency of crosslinking in both cases. The changes in efficiency are attributed to the influence of the reaction variables (in particular, the concentration of rubber-soluble complexes of zinc laurate with zinc benzothiazolyl mercaptide) on the structure and subsequent reactions of initially formed polysulfidic crosslinks.

INTRODUCTION

In 1952 Barton and Hart[1] demonstrated convincingly that the full realization of the crosslinking potential of sulfur in the vulcanization of natural rubber (NR) accelerated by 2-mercaptobenzothiazole (MBT) requires the correct choice of reaction temperature and time and of the relative concentrations of sulfur, MBT, and the vulcanization activators zinc oxide and fatty acid. For a given mix formulation the efficiency with which sulfur is utilized for crosslinking the NR increases as the vulcanization temperature is decreased within the range 160–90°C. and as the reaction time is increased up to the point of modulus reversion. At a given temperature and sulfur concentration maximum utilization of sulfur for crosslinking is achieved only when certain critical minimum concentrations of MBT, zinc oxide, and fatty acid (lauric acid) are present. Depletion of any one of these reactants reduces the crosslinking potential of the sulfur. Complementary kinetic studies[2-4] have shown that the rates of sulfur *reaction* and of crosslink formation in this vulcanization system increase with increasing concentrations of MBT (up to a limiting rate value) and of zinc soap.

Barton[5] later studied the relationship between the degree of crosslinking, sulfur combined in the network, and sulfur present as zinc sulfide, for vulcanizates obtained by use of vulcanization conditions leading to efficient utilization of sulfur for crosslinking (viz., in weight per weight, NR 100, sulfur 0.125–1.25, MBT 2, zinc oxide 10, lauric acid 10, the mix vulcanized for 64 hr. at 100°C.). The degree of crosslinking, $(2M_c)^{-1}$, where M_c is the number-average molecular weight of rubber chains between crosslinks, was obtained from measurements of the "equilibrium" stress at 100% extension and by means of eq. (1), derived from the statistical theory of rubberlike elasticity:

$$f = \rho R T A_0 \dot{M}_c{}^{-1}(\lambda - \lambda^{-2}) \tag{1}$$

where f is the force required to extend the sample of density ρ and original cross-sectional area A_0 to an extension ratio λ, R is the gas constant, and T the absolute temperature. It was concluded that, under the efficient vulcanization conditions used, the sulfur combined in the network is present predominantly as monosulfide crosslinks, and the crosslinking process and the formation of zinc sulfide are closely related reactions.

We now report an extension and refinement of these pioneering studies of Barton and Hart.[1,5] On the basis of their findings and of preliminary studies of our own, not reported here, the mix formulation chosen for the present work was NR 100, sulfur 1.5, MBT 1.5, zinc oxide 5.0, and lauric acid variable. This mix has the potentiality of making very efficient use of sulfur for crosslinking purposes, provided due attention is paid to the level of lauric acid and to the temperature and time of vulcanization. The effect of changes in these three reaction variables has been investigated in terms of (1) the degrees of physical and *chemical* crosslinking attained by the vulcanizate network, (2) the pattern of sulfur combination in the network as reflected by the values of the crosslinking efficiency of sulfur, E, which is defined as the number of sulfur atoms required to be combined in the network to produce one *chemical* crosslink, and (3) the number of molecules of zinc sulfide formed for each chemical crosslink present in the network; this quantity is designated F in the following discussion.

The present work is a refinement of the earlier work[1,5] in the following respects. First, it does not assume, as is implied by eq. (1), an identity between the chemical crosslinks inserted into the network and the crosslinks manifested physically in stress–strain measurements. Instead, use is made of the calibration developed by Mullins[6,7] and Moore and Watson,[8] which relates the chemical and physically manifested crosslinks in peroxide-vulcanized NR networks and which makes allowance for physical entanglements and chain ends in the networks. Second, allowance is made for the stiffening effect of the large amount of zinc laurate present in vulcanizates derived from those mixes containing 10 parts lauric acid per 100 parts rubber. Third, the contributions of other particulate material and rubber-soluble extra-network material to the experimentally determined elastic

modulus is allowed for using the procedure described in Part V of this series.[9]

These refinements permit a more realistic quantitative description to be given than was possible previously,[1,5,10,11] of the chemistry of the cross-linking process, of the structural features of the network, of the significance of zinc sulfide formation, and of how all of these are influenced by the reaction variables specified above.

MATERIALS AND EXPERIMENTAL METHODS

Materials

The NR was RSS1 (Yellow Circle), which was homogenized on a two-roll mill under conditions leading to minimal molecular breakdown. Two samples of raw NR were used, the analytical details of which are given in Table I. Sieved flowers of sulfur (85-mesh sieve) were used throughout. The MBT was Vulcafor MBT (Imperial Chemical Industries Ltd.). The zinc oxide was No. 3 Normal French Process grade, kindly supplied by Amalgamated Oxides (1939) Ltd. The lauric acid was standard grade, supplied by British Drug Houses Ltd.

TABLE I
Analyses of Raw NR (RSS1, Yellow Circle)

Sample no.	N,[a] wt.-%	S,[b] wt.-%	Ash, wt.-%	Loss on acetone extraction,[c] wt.-%	Fatty acid (expressed as lauric acid),[d] wt.-%
1	0.393	0.025	0.25	2.84	0.60
1	0.410	0.027	0.25	2.84	0.60
2	0.427	0.029	0.29	3.39	0.75
2	0.433	0.029	0.29	3.39	0.75

[a] Kjeldahl method on 500 mg. samples (see Part III of this series[12]).

[b] Determined on 300 mg. samples with the Ba^{2+}/EDTA complexometric titration method described in Part I of this series.[13]

[c] Loss in weight of NR sample (5 g.) resulting from extraction with refluxing acetone for 48 hr. in the dark under nitrogen.

[d] Determined[14] on acetone extract from loss of weight of NR sample.[c]

Preparation of Vulcanizates

Mixes (Table II) were prepared by standard mixing procedures on a two-roll mill under controlled conditions which resulted in closely similar, initial number-average molecular weights ($\bar{M}_n$) of the rubber, thus minimizing variations in vulcanizate properties. Values of $\bar{M}_n$ were derived from values of the limiting viscosity number, $[\eta]_{benzene}$ (dl./g.), at 25°C. of the rubber hydrocarbon component of the mixes, by using the expression[15]

$$[\eta]_{benzene} \text{ (dl./g.)} = 2.29 \times 10^{-7} \bar{M}_n^{1.33} \tag{2}$$

TABLE II

Mix Formulations and Vulcanization Temperatures Used in Preparation of MBT-Accelerated NR–Sulfur Vulcanizates

				Mix no.						
						E				
	A	B	C	D	1	2	3	4	5	6
Parts, wt.										
NR (sample 1)	100		—				—			
NR (sample 2)	—		100				100			
Sulfur	1.5		1.5				1.5			
MBT	1.5		1.5		0.3	0.4	0.5	0.6	0.8	1.1
Zinc oxide	5.0		5.0				5.0			
Lauric acid	10.0		1.0				10.0			
Vulcanization temp., °C.	100	140	100	140			100			
Dimensions of molded sheets, cm.	18 × 18 × 0.2	30 × 30 × 0.2	18 × 18 × 0.2	30 × 30 × 0.2			18 × 18 × 0.1			

The viscosity measurements were made as soon as possible after mixing. Vulcanization was effected at 140 ± 0.25°C. or at 100 ± 1°C., to produce sheets either 1 or 2 mm. in thickness. Molds were cooled rapidly before opening of the press at the conclusion of the vulcanization period. A 2.5 cm. perimeter of each sheet was discarded, and chemical analyses, determinations of the elastic parameters C_1 and C_2 of the Mooney-Rivlin equation (see later), and equilibrium swelling measurements in n-decane were determined on the central 12 cm. square of the sheet.

Chemical Analysis of Vulcanizates

Except where stated otherwise in the tables, inorganic sulfide sulfur (S^{2-}), present as zinc sulfide in the vulcanizate, was determined on 1 g. samples of the *unextracted* vulcanizates milled to a fine crumb.[16]

Sulfur combined in the *network*, S_c, was determined on extracted samples of the vulcanizate. A variety of extraction procedures was investigated, to establish the best conditions for removal from the vulcanizate of all extra-network material (other than zinc oxide and zinc sulfide) without changing the physical state of the network (i.e., the number and distribution of sulfidic crosslinks). Variables studied were (1) sample form (2.5 × 1.25 cm. strips, 1 × 0.1 cm. strips, and thin sheets or crumb produced by cold milling), (2) extraction solvent (hot acetone and hot azeotropic mixture of acetone and chloroform and methanol, 352:291:274 ml.) of b.p. 57.5°C.,[17] and (3) extraction time (24, 50, and 96 hr.). The conditions finally chosen were continuous hot extraction of 1 × 0.1 cm. strips for 96 hr. with the azeotrope under nitrogen in the dark. The extracted samples were freed from solvent under vacuum at room temperature. The weight percent of extracted material was determined from the weights of the sample before and after extraction.

The sum $[S_c + S^{2-}]$ in the extracted vulcanizate was determined on ca. 300 mg. samples by the Ba^{2+}/EDTA complexometric titration method described in Part I.[13] Values of $[S_c + S^{2-}]$ were corrected for the sulfur content of the raw rubber (Table I), and $[S_c]$ was then obtained by difference of the corrected $[S_c + S^{2-}]$ value of the extracted vulcanizate and the $[S^{2-}]$ value of the original unextracted vulcanizate after allowing for the weight loss on extraction.

Physical Characterization of Vulcanizates and Determination of the Degree of Chemical Crosslinking, $(2M_{c,\,chem}^{RH})^{-1}$, of the Rubber Hydrocarbon Component of the Vulcanizate Networks

Low-Extension Modulus and Tensile-Strength Measurements. Values of MR 100, the relaxed modulus at 100% extension, were determined[18] on dumbbell test pieces cut from the molded sheets. Tensile strengths were determined on similar test pieces.[19]

Stress-Strain Measurements. Initially these were determined on strips by the method described by Mullins and Turner[20] (data of Table VI).

Subsequently, stress–strain measurements were made on an instrument designed in these laboratories.[21] The latter method involves measurement of the tension in a parallel-sided strip held at a series of predetermined and precisely known extensions, according to a strict schedule of time intervals (3 min.) between each extension increment and measurement of tension. Measurements were made at constant temperature and corrected to 25°C. The data were treated according to the Mooney-Rivlin equation,

$$f = 2A_0(\lambda - \lambda^{-2})(C_1 + \lambda^{-1}C_2) \tag{3}$$

where f is the force required to extend a sample having an original cross-sectional area A_0 to an extension ratio λ, and where C_1 and C_2 are parameters characterizing the vulcanizate. A_0 was determined from a series of three to four width and thickness measurements made along the length of the strip. The results were analyzed by plotting $f[2A_0(\lambda - \lambda^{-2})]^{-1}$ against λ^{-1}. C_1 was obtained by extrapolating the linear portion of the curve to $\lambda^{-1} = 0$, and C_2 was derived from the slope of the linear portion.

Vulcanizates from mixes C and D (Table II) gave plots with sufficiently extensive linear portions to permit reliable values of C_1 and C_2 to be obtained as described above. Where these apply to the original raw vulcanizates, they are designated $C_{1,RV}$ and $C_{2,RV}$, respectively. By using the methods of Part V of this series[9] values of $C_{1,RV}$ were converted into values of $C_{1,ERM}$, that is, the C_1 pertaining to the partially collapsed vulcanizate network devoid of filler and rubber-soluble diluent; $C_{1,ERM}$ was then converted into $C_{1,RH}$, that is, the C_1 of the rubber hydrocarbon component of the network. Values of $C_{1,RH}$ were then used to obtain values of $(2M_{c,\text{chem}}^{RH})^{-1}$ (g.-mole chemical crosslinks per g. rubber hydrocarbon in the network) by means of the expression[7]

$$C_{1,RH} = [\rho RT(2M_{c,\text{chem}}^{RH})^{-1} + 0.78 \times 10^6]$$
$$\times (1 - 2.3M_{c,\text{chem}}^{RH} \bar{M}_n^{-1}) \text{ dyne cm.}^{-2} \tag{4}$$

where ρ is the density of the rubber hydrocarbon (0.915 g. ml.$^{-1}$ at 25°C.), $M_{c,\text{chem}}^{RH}$ is the number-average molecular weight of the rubber hydrocarbon chain segments between adjacent chemical crosslinks, $\bar{M}_n$ is the number-average molecular weight of the primary rubber molecules as they exist in the network, R is the gas constant, and T is the absolute temperature. The values of $\bar{M}_n$ used in eq. (4) are identified with $\bar{M}_n$ of the rubber hydrocarbon component of the mixes prior to vulcanization; that is, it is assumed in the absence of evidence to the contrary that no scission of the primary rubber molecules occurs during the vulcanization reaction.

Values of $C_{1,RH}$ derived from values of $C_{1,RV}$ of the vulcanizates from mixes C and D (Table II) were shown to be reliable by their demonstrated near-equivalence with $C_{1,RH}$ values obtained from extracted, partially swollen samples (which exhibited much lower C_2 values); see Table III.

For the raw vulcanizates from mixes A, B, and E (Table II) plots of $f[2A_0(\lambda - \lambda^{-2})]^{-1}$ versus λ^{-1} were curved throughout the whole range of

TABLE III
Effect of Extraction and Partial Swelling on Stress–Strain Properties of MBT-Accelerated NR–Sulfur Vulcanizates (Repeat Vulcanization of Mix D, Table II)

Stress–strain properties at 25°C., dyne cm.$^{-2}$ $\times$ 10^{-6}

Vulcaniz. time at 140°C., min.	$C_{1,RV}$	$C_{2,RV}$	$C_{1,RH}$ (computed from $C_{1,RV}$)	C_1 of azeotrope-extracted and partially swollen[a] vulcanizate	C_2 of azeotrope-extracted and partially swollen[a] vulcanizate	$C_{1,RH}$ (computed from C_1 of azeotrope-extracted and partially swollen vulcanizate)
60	0.96	0.97	0.96	0.89	0.25	0.92
240	0.88	0.96	0.88	0.80	0.15	0.83

[a] Samples were swollen in a 1:1 (vol./vol.) mixture of liquid paraffin (Nujol) and light petroleum (b.p. 40–60°C.), and then the light petroleum was removed at room temperature under vacuum. Volume swelling ratio of the 60 min. vulcanizate is 0.396; of the 240 min. vulcanizate, 0.380.

extensions (Fig. 1), and thus meaningful values of $C_{1,\text{RV}}$ and $C_{2,\text{RV}}$ could not be obtained therefrom.   Figure 1 shows that the stress–strain characteristics of these raw vulcanizates, which contain a high loading of zinc laurate and complexes of zinc laurate with the zinc mercaptide (ZMBT) derived
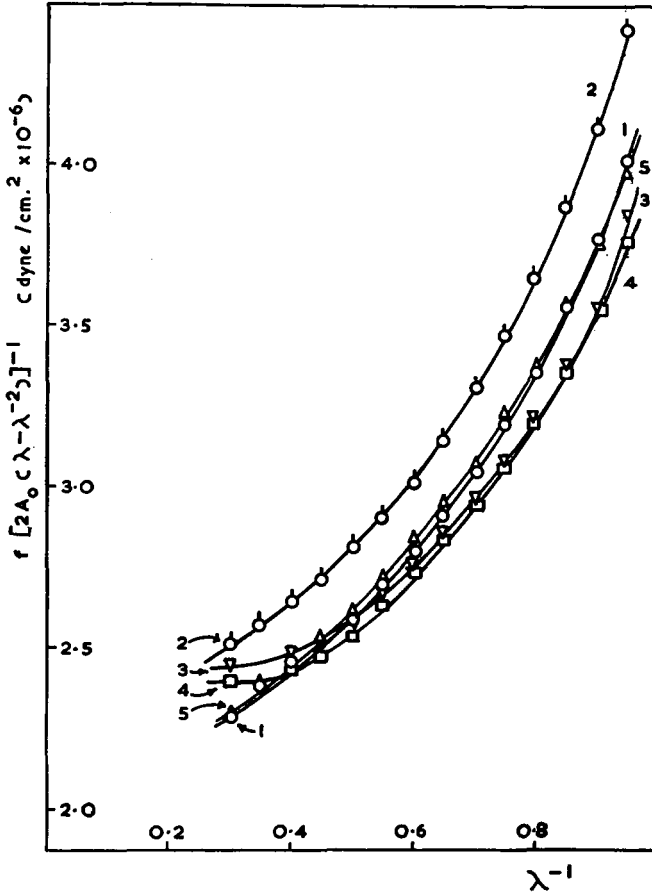

Fig. 1. Dependence of stress–strain properties on history of vulcanizate sample from mix E; 0.6 parts sulfur per 100 rubber, vulcanized for 144 hr. at 100°C. (Table II): (1) raw vulcanizate measured 15 days after vulcanization; (2) raw vulcanizate measured 72 days after vulcanization.   (3) remeasurement of sample of curve 2, i.e., second extension; (4) remeasurement of sample of curve 1, i.e., second extension; (5) raw vulcanizate rested at room temperature for 72 days, then heated for 1 hr. at 100°C. in vacuo, stored at room temperature for 24 hr. and then measured.

from the MBT, are sensitive to the history of the sample.   Thus, (a) the vulcanizate stiffens with increasing time of resting at room temperature after vulcanization (compare curves 1 and 2, Fig. 1), (b) the vulcanizate exhibits a typical Mullins stress-softening effect on repeated extension

(compare curves *1* and *4* and curves *2* and *3*, Fig. 1), (*c*) the magnitude of (*b*) increases with the time interval between the vulcanization and testing of the vulcanizate (compare the difference between curves *1* and *4* with that between curves *2* and *3*, Fig. 1), and (*d*) heating the rested vulcanizate for 1
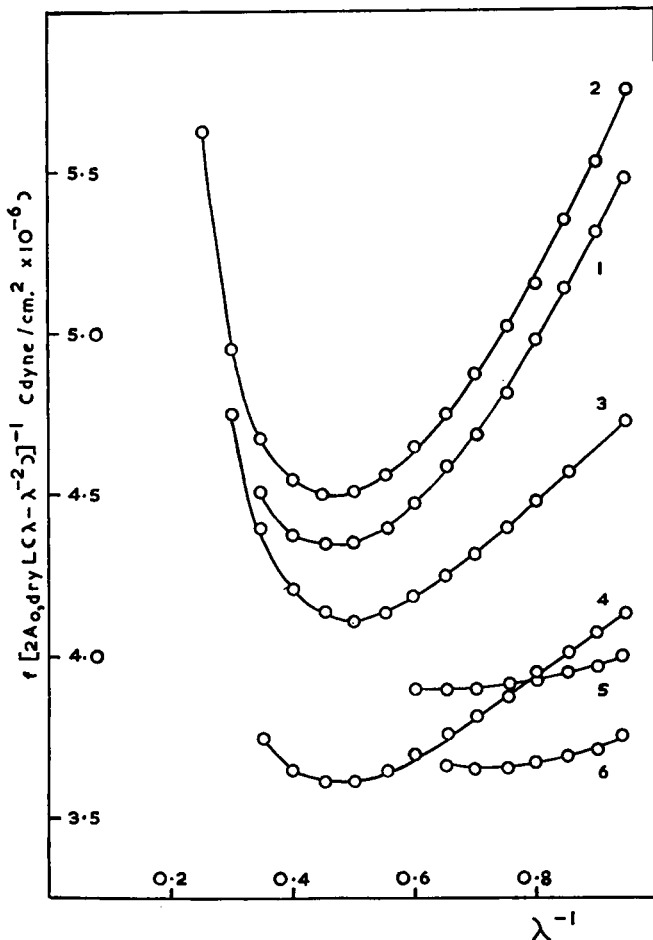

Fig. 2. Effects of extraction and swelling on stress–strain properties of vulcanizate from mix A; vulcanized for 144 hr. at 100°C. (Table II): (*1*) raw vulcanizate measured 56 days after vulcanization; (*2*) raw vulcanizate measured 70 days after vulcanization; (*3*) measurement of azeotrope-extracted vulcanizate; (*4*) measurement of vulcanizate after azeotrope extraction and ether–hydrochloric acid treatment; (*5*) measurement of azeotrope-extracted and partially swollen vulcanizate (sample swollen in liquid paraffin to linear swelling ratio L of 1.248); (*6*) as curve *5*, but with $L = 1.140$.

hr. at 100°C. under vacuum reduces markedly the stiffening effect (*d*) (compare curves *2* and *5*, Fig. 1). The effects (*b*) and (*d*) indicate that the stiffening effect (*1*) is not due to post-vulcanization crosslinking of the rubber network at room temperature; this is supported by the fact that the vul-

canization conditions used (144 hr. at 100°C.) for the vulcanizate discussed here are those leading to maximum crosslinking (Table VIII; see also Fig. 3). The curvature shown by the Mooney-Rivlin plots and the observed stress-softening effect on repeated stretching to a low extension ratio are characteristic of reinforced vulcanizates, and we attribute them and the slow stiffening of the vulcanizate on resting at room temperature to the presence of the zinc laurate and its complexes with ZMBT, which slowly crystallize and produce some solid "structure." The effect (d) is consistent with this view.

The effects (b-d) were not exhibited by the vulcanizates from mixes C and D. However, undercured vulcanizates from these mixes did stiffen slowly on resting at room temperature; for example, the vulcanizate prepared from mix D by heating for 10 min. at 140°C. showed a 48% increase in $C_{1,\mathrm{RV}}$ on standing for 2 years at room temperature. In this case the stiffening effect is due to slow additional crosslinking at room temperature, since heating the stiffened specimen for 1 hr. at 100°C. under vacuum caused a further increase in $C_{1,\mathrm{RV}}$ of 3%. The $C_{1,\mathrm{RV}}$ data obtained for the vulcanizates from mixes C and D are free from error caused by this post-vulcanization crosslinking, since they were all measured within 10 days of preparation.

Attempts to obtain reliable values of C_1 and C_2 for vulcanizates derived from mixes A, B, and E, which contained high levels of lauric acid, 10 pphr (Table II), were made therefore as follows. First, the raw vulcanizates were freed from zinc laurate, its complexes with ZMBT, and other extra-network material (apart from zinc oxide and zinc sulfide) by extraction with the azeotropic mixture, as described above. Figure 2 shows that the Mooney-Rivlin plot of the extracted vulcanizate (Fig. 2, curve 3) has an appreciable linear portion, from which C_1 and C_2 values can be obtained. Second, the extracted vulcanizate was freed from zinc oxide and zinc sulfide by treatment with ether–hydrochloric acid, as described in Part IV of this series;[22] an extensive linear portion of the Mooney-Rivlin plot is observed for the sample which is now literally the vulcanizate *network* (Fig. 2, curve 4). There was no advantage in attempting to determine C_1 and C_2 values on partially swollen samples of the azeotrope-extracted vulcanizate, since the early intrusion of finite extensibility effects causes upward curvature of the plot at low extensions (Fig. 2, curves 5 and 6). Values of C_1 derived from curves 3 and 4 in Figure 2 were used indirectly in conjunction with equilibrium swelling measurements, to obtain estimates of $(2M_{c,\,\mathrm{chem}}^{\mathrm{RH}})^{-1}$ for the whole range of vulcanizate networks derived from mixes A, B, and E (see below).

Swelling Measurements. Equilibrium values of v_r, the volume fraction of rubber network in the swollen rubber network, were determined in n-decane at 25°C. in the dark; equilibrium swelling was achieved within the 48 hr. swelling period used. Values of v_r were computed from the measured weights of the original, swollen, and deswollen samples, as described in Part V of this series.[9]

TABLE IV

Estimation of χ for Vulcanizate Networks Derived from MBT-Accelerated NR–Sulfur System

(Repeat Vulcanization of Mix A, Table II)

Vulcan. time at 100°C., hr.	Wt. loss on extraction of RV with azeotrop. mixt.,[a] %	Wt. loss on extraction of RV with azeotrop. mixt. followed by ether–hydrochloric acid treatment, %	Stress–strain measurements: C_1 at 25°C., dyne/cm.^{2} $\times 10^{-6}$			Equilibrium swelling measurements: v_r at 25°C. in n-decane of vulcanizate networks		Vulcanizate network–n-decane interaction parameter χ	
			C_1 of extracted vulcanizate	$C_{1,\mathrm{ERM}}$ computed from C_1 of extracted vulcanizate	C_1 of extracted and ether–hydrochloric-acid-treated vulcanizate, i.e. $C_{1,\mathrm{ERM}}$	v_r of extracted vulcanizate (coord. for filler)	v_r of extracted and ether–hydrochloric-acid-treated vulcanizate	χ derived from measurements on extracted vulcanizate	χ derived from measurements on extracted and ether–hydrochloric-acid-treated vulcanizate
3	14.0	19.2	0.48	0.47	—[b]	0.171	—[b]	0.425	—
24	12.6	16.1	2.42	2.36	2.12	0.330	0.307	0.410	0.395
72	11.4	—[b]	2.85	2.76	2.77	0.363	0.351	0.430	0.410
144	11.4	—[b]	3.15	3.06	2.90	0.368	0.354	0.415	0.405
								Mean: 0.413	(S.D.: 0.011)

[a] RV, raw vulcanizate.

[b] Not measured.

Equilibrium values of v_r and values of $C_{1,\mathrm{ERM}}$ were used to estimate values of the rubber-network–swelling-liquid interaction parameter χ of the Flory–Rehner equation,

$$-\ln\,(1\,-\,v_r)\,-\,v_r\,-\,\chi v_r^2\,=\,2C_{1,\mathrm{ERM}}V_0 v_r^{1/3}[RT]^{-1} \tag{5}$$

where V_0 is the molar volume of the swelling liquid, and the other symbols have their previously defined significance.

Estimates of $(2M_{c,\,\mathrm{chem}}^{\mathrm{RH}})^{-1}$ for the networks derived from mixes A, B, and E (Table II) were obtained indirectly from the equilibrium v_r values as follows. Measured or computed values of $C_{1,\mathrm{ERM}}$ and the measured values of v_r of rubber networks from a range of vulcanizates of mix A were used in conjunction with eq. (5) to obtain a value of χ (Table IV). This value of χ and the experimentally determined equilibrium values of v_r of the rubber networks of vulcanizates derived from mixes A, B, and E (Table II) then yielded $C_{1,\mathrm{ERM}}$ values [eq. (5)], from which were obtained estimates of $(2M_{c,\,\mathrm{chem}}^{\mathrm{RH}})^{-1}$ via $C_{1,\mathrm{RH}}$ values and eq. (4) by the procedure of Part V.[9]

Determination of E and F Values of Vulcanizate Networks. These quantities are defined as

$E\,=\,[\mathrm{S}_c]/(2M_{c,\,\mathrm{chem}}^{\mathrm{RH}})^{-1}\,=\,$ [(g.-atom sulfur combined)/(g. rubber hydrocarbon in network)]/[(g.-mole chemical crosslinks)/(g. rubber hydrocarbon in network)]

$=\,$ (no. sulfur atoms combined in network)/(chem. crosslink present)

$F\,=\,[\mathrm{S}^{2-}]/(2M_{c,\,\mathrm{chem}}^{\mathrm{RH}})^{-1}\,=\,$ [(g.-ion of sulfide formed)/(g. rubber hydrocarbon in network)]/[(g.-mole chemical crosslinks)/(g. rubber hydrocarbon in network)]

$=\,$ (no. sulfide ions, as zinc sulfide, formed)/(chem. crosslink present in network)

and were determined from the experimental or computed values of $[\mathrm{S}_c]$, $[\mathrm{S}^{2-}]$, and $(2M_{c,\,\mathrm{chem}}^{\mathrm{RH}})^{-1}$.

RESULTS AND DISCUSSION

Table V records the data for low-extension modulus (MR 100) and tensile strength of all the vulcanizates reported here. The relationship between vulcanization method, vulcanizate structure, and tensile strength of these and other NR gum vulcanizates has been discussed in detail elsewhere[23] and will not be considered further here. The MR 100 data (Table V) are consistent with the findings of Barton and Hart[1] referred to in the Introduction.

More precise descriptions of the physical and chemical structural features of the vulcanizate networks and their time-dependent nature are given in Tables VI–IX.

Figure 3 clearly demonstrates that the crosslinking potential of sulfur in the presence of fixed amounts of MBT and zinc oxide is increased by decreasing the vulcanization temperature within the range 140–100°C. (compare curve A with B and C with D, Fig. 3) and, more particularly, by
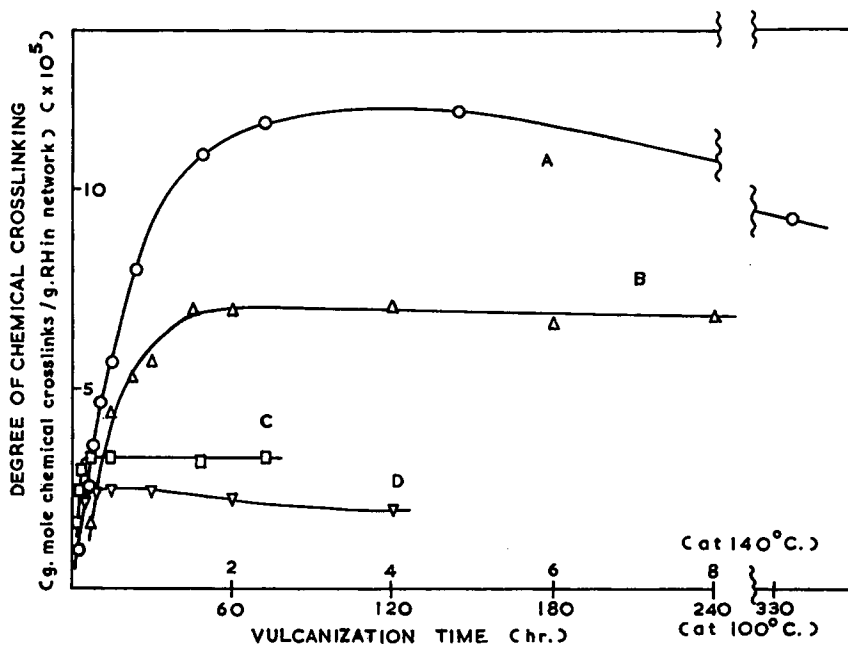
Fig. 3. Relationship between degree of chemical crosslinking $(2M_{,c,\text{chem}}^{\text{RH}})^{-1}$ and vulcanization time of mixes A–D (Table II).

increasing the amount of lauric acid in the mix from 1 to 10 pphr (compare curve A with C and B with D, Fig. 3). A fivefold increase in the yield of chemical crosslinks is achieved within the imposed limits of these two reaction variables (compare curve A with D, Fig. 3). This is reflected in changes in the pattern of sulfur combination in the various networks, as revealed by the E values of the networks, i.e. the number of sulfur atoms combined in the network per chemical crosslink present (Fig. 4 and Tables VII and IX). This feature and its implications will be illustrated by reference to the vulcanization systems A and D.

For system D the initially high value of E of 14 network-combined sulfur atoms per crosslink and its progressive increase in magnitude to 19 with increasing reaction time imply a relatively complex network structure, which becomes more complex still as reaction proceeds. This is confirmed by treatment of the networks with the chemical probe triphenylphosphine,[22,24] which has shown that throughout the whole reaction range much of the sulfur present (at least 47–63%, depending on reaction time) is combined in groupings external to the crosslinks, i.e., in main-chain modifications. Experiments[11,25] with the "model" olefins trans-2,6-dimethyl-2,6-octadiene and 2-methyl-2-pentene have shown these modifications to be five- and six-membered cyclic sulfides together with pendent groups of the type
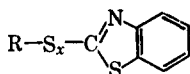
TABLE V
Modulus (MR 100) and Tensile-Strength Data for Vulcanizates
Derived from MBT-Accelerated NR–Sulfur System (Mixes A–E, Table II)

Cure time	MR 100, kg./cm.²	Tensile strength, kg./cm.²	Cure time	MR 100, kg./cm.²	Tensile strength, kg./cm.²
Mix A: hr. at 100°C.			Mix C: hr. at 100°C.		
2	2.4, 2.5	64, 65, 104	2	3.3, 3.9	150, 258
3	3.2, 3.3	130, 135, 151	3	4.9, 5.3	256
4	4.5, 5.0	218, 221, 249	4	6.1, 6.2	245, 250, 290
6	5.6, 5.7	275, 281, 282	8	6.6, 6.6	210, 240, 283
8	7.3, 7.9	242, 290, 290	16	6.0, 6.0	228, 245, 270
10	8.2, 8.6	281, 300, 301	48	6.1, 6.5	235, 245, 265
16	9.3, 9.5	286, 296, 300	72	6.0, 6.1	205, 230, 252
24	11.1, 11.6	262, 267, 282			
48	14.8, 15.0	199, 228, 237			
72	16.8, 16.9	187, 193			
144	16.6, 16.9	107, 135, 147			
336	16.3; 16.8	123, 135, 143			

Mix B:

min. at 140°C.		
5	1.6, 1.8	15, 15, 24
10	3.5, 3.8	173, 180, 190
15	5.0, 5.2	247, 253, 267
30	7.2, 7.3	280, 281, 290
45	8.0, 8.2	274, 274, 286
60	8.8, 8.9	250, 262, 268
90	9.7, 9.8	195, 212, 231
120	10.4, 10.5	216, 223, 231
240	11.0, 11.0	178, 212, 228
360	10.4, 10.8	154, 172, 203
480	9.2, 9.5	170, 187, 199

Mix E:

S (pphr.), 144 hr. at 100°C.		
0.4	6.8, 7.0	221, 238, 239
0.5	8.0, 8.1	228, 240, 241
0.6	9.1, 9.2	230, 250, 251

Mix D:

min. at 140°C.		
10	4.9, 4.9	203, 204, 212
15	5.4, 5.6	253, 262, 268
30	5.6, 5.8	193, 207, 217
60	5.0, 5.2	178, 192, 199
120	5.0, 5.2	174, 177, 219
240	5.0, 5.2	143, 165

Mix E:

S (pphr.), 336 hr. at 100°C.		
0.3	5.6, 5.7	212, 218, 222
0.5	8.0	199, 223, 232
0.8	10.0	181, 195, 197
1.1	11.8	171, 176, 191

TABLE VI

Physical Characterization of Vulcanizate Networks Derived from MBT-Accelerated NR–Sulfur System (Mixes C and D, Table II) and Estimates of the Degrees of Chemical Crosslinking of the Rubber Hydrocarbon Component of the Networks, $(2M_{c,chem}^{RH})^{-1}$

Cure time	$[\eta]_{benz.}$[a] dl./g.	$\bar{M}_n$[b] $\times 10^{-5}$	Elastic constants, dynes/cm.² $\times 10^{-6}$		Temp.,[c] °C.	$C_{1,ERM}$[d]	v_r°[e]	x	$C_{1,RH}$[f]	$(2M_{c,chem}^{RH})^{-1}$ ($\times 10^4$)[g]
			$C_{1,RV}$	$C_{2,RV}$						
Mix C: hr. at 100°C.										
2	3.16, 3.24	2.4	0.78	0.90	24	0.76	0.2269	0.45	0.79	0.16
3	3.02, 3.07	2.3	1.04	1.10	20.5	1.01	0.2610	0.46	1.05	0.24
4	2.92	2.2	1.14	1.10	21	1.12	0.2657	0.45	1.15	0.29
8	2.96, 2.99	2.2	1.27	1.10	22	1.24	0.2769	0.45	1.28	0.33
16	2.92, 2.96	2.2	1.26	1.02	21.5	1.23	0.2748	0.45	1.27	0.33
48	2.82, 2.86	2.2	1.25	1.03	23	1.21	0.2756	0.45	1.25	0.32
72	2.54, 2.54	2.0	1.23	1.07	24	1.20	0.2763	0.455	1.24	0.33
Mix D: min. at 140°C.										
10	3.02, 3.07	2.3	0.98	0.93	23	0.95	0.2471	0.445	0.98	0.22
15	2.92	2.2	1.04	1.01	21	1.01	0.2578	0.455	1.04	0.24
30	2.96, 2.99	2.2	1.04	1.00	21	1.01	0.2557	0.45	1.04	0.24
60	2.92, 2.96	2.2	1.03	1.00	23	0.99	0.2514	0.445	1.03	0.24
120	2.82, 2.86	2.2	0.97	0.96	24.5	0.93	0.2477	0.45	0.96	0.22
240	2.54, 2.54	2.0	0.87	0.94	19.5	0.85	0.2434	0.46	0.88	0.20

[a] $[\eta]_{benz.}$ of rubber hydrocarbon component of mix at 25°C.

[b] $\bar{M}_n$ of rubber hydrocarbon component of mix.

[c] Temperature of measurement of $C_{1,RV}$ and $C_{2,RV}$.

[d] In dynes/cm.² $\times 10^{-6}$, at 25°C.

[e] Equilibrium v_r of network in n-decane at 25°C.

[f] In dynes/cm.² $\times 10^{-6}$, at 25°C.

[g] Gram-mole chemical crosslinks per gram rubber hydrocarbon in the network.

TABLE VII

Chemical Characterization of Vulcanizate Networks Derived from MBT-Accelerated NR–Sulfur System (Mixes C and D, Table II)

Cure time	$[S_c + S^{2-}]$ of extracted vulcanizate, wt.-%	Wt. loss on extraction of raw vulcanizate, %	$[S_c + S^{2-}]$ of raw vulcanizate,[a] wt.-%	$[S^{2-}]$ of raw vulcanizate, wt.-%	$[S_c]$ ($\times 10^4$)[b]	$[S^{2-}]$ ($\times 10^4$)[c]	$(2M_{c,\text{chem}}^{RH})^{-1}$ ($\times 10^4$)[d]	E[e]	F[f]
Mix C: hr. at 100°C.									
2	0.70	6.81	0.62	0.106	1.80	0.37	0.16	11.2	(2.3)
3	1.06	6.48	0.96	0.124	2.97	0.44	0.24	12.3	1.8
4	1.23	6.43	1.12	0.150	3.41	0.53	0.29	12.0	1.9
8	1.46	5.89	1.34	0.183	4.08	0.64	0.33	12.5	2.0
16	1.51	5.60	1.40	0.199	4.22	0.70	0.33	13.0	2.2
48	1.53	5.52	1.42	0.242	4.15	0.85	0.32	13.0	2.7
72	1.56	5.44	1.45	0.273	4.15	0.96	0.33	12.8	3.0
Mix D: min. at 140°C.									
10	1.05	4.47	0.97	0.104	3.06	0.37	0.22	13.9	1.7
15	1.38	5.76	1.27	0.145	3.94	0.51	0.24	16.2	2.1
30	1.52	(8.06)	1.37	0.186	4.15	0.66	0.24	17.3	2.7
60	1.53	5.49	1.42	0.246	4.12	0.87	0.24	17.5	3.7
120	1.52	5.62	1.40	0.284	3.94	1.00	0.22	17.9	4.6
240	1.53	6.34	1.40	0.322	3.80	1.13	0.20	18.6	5.6

[a] Corrected for the sulfur content of the raw rubber.
[b] Gram-atom of sulfur per gram rubber hydrocarbon in the network.
[c] Gram-ion of sulfide per gram rubber hydrocarbon in the network.
[d] Gram-mole chemical crosslinks per gram rubber hydrocarbon in the network.
[e] Number of sulfur atoms combined in the network per chemical crosslink present.
[f] Number of sulfide ions formed per chemical crosslink present in the network.

TABLE VIII

Physical Characterization of Vulcanizate Networks Derived from MBT-Accelerated NR–Sulfur System (Mixes A, B, and E, Table II) and Estimates of Degrees of Chemical Crosslinking of Rubber Hydrocarbon Component of Networks, $(2M_{c,chem}^{RH})^{-1}$

Cure time	$[\eta]_{benzene}$ rub. hydrocarbon compn. of mix at 25°C., dl./g.	$\bar{M}_n$ rub. hydrocarbon compn. of mix × 10⁻⁵	Equil. v_r of network in n-decane at 25°C.	$C_{1,ERM}$ at 25°C.,[a] dyne/cm.² × 10⁻⁶	$C_{1,RH}$ at 25°C., dyne/cm.² × 10⁻⁶	$(2M_{c,chem}^{RH})^{-1}$ (× 10⁴)[b]
Mix A: hr. at 100°C.						
3	3.09, 3.11	2.3	0.1554	0.42	0.46	0.10
6	2.73, 2.85	2.1	0.2259	0.96	1.05	0.26
8	2.94, 2.97	2.2	0.2527	1.24	1.36	0.36
10	2.99, 3.03	2.3	0.2736	1.50	1.64	0.47
16	3.33, 3.40	2.5	0.2902	1.72	1.88	0.57
24	2.94, 3.03	2.2	0.3214	2.21	2.42	0.80
48	2.93, 2.96	2.2	0.3538	2.82	3.08	1.09
72	3.18, 3.43	2.4	0.3617	2.98	3.26	1.17
144	3.09, 3.09	2.3	0.3646	3.05	3.33	1.20
336	2.80, 2.81	2.1	0.3359	2.48	2.71	0.93
Mix B: min. at 140°C.						
10	3.09, 3.11	2.3	0.1970	0.70	0.77	0.16
15	3.12, 3.14	2.3	0.2285	0.98	1.08	0.25
30	2.94, 2.97	2.2	0.2679	1.43	1.56	0.44
45	2.99, 3.03	2.3	0.2836	1.63	1.78	0.53
60	3.09, 3.09	2.3	0.2898	1.72	1.88	0.57
90	3.23, 3.23	2.4	0.3092	2.01	2.20	0.70
120	3.08, 3.13	2.3	0.3086	2.00	2.19	0.70
240	3.05, 3.21	2.3	0.3104	2.03	2.22	0.71
360	2.73, 2.85	2.1	0.3033	1.92	2.10	0.67
480	3.18, 3.43	2.4	0.3067	1.97	2.16	0.69

Mix E:

S (pphr.) 144 hr. at 100°C.

0.4	2.82, 2.83	2.1	0.2469	1.18	1.29	0.34
0.5	2.57, 2.57	2.0	0.2621	1.35	1.48	0.42
0.6	2.35, 2.38	1.9	0.2747	1.51	1.66	0.50

Mix E:

S (pphr.) 336 hr. at 100°C.

0.3	2.56, 2.56	2.0	0.2211	0.91	1.00	0.24
0.5	2.28, 2.31	1.8	0.2469	1.18	1.29	0.35
0.8	2.59, 2.59	2.0	0.2825	1.62	1.78	0.54
1.1	2.22, 2.22	1.8	0.3036	1.93	2.12	0.70

[a] Derived from v_r values and with χ = 0.41.

[b] Gram-mole chemical crosslinks per gram rubber hydrocarbon in network.

TABLE IX

Chemical Characterization of Vulcanizate Networks Derived from MBT-Accelerated NR–Sulfur System (Mixes A, B, and E, Table II)

Cure time	$[S_c + S^{2-}]$ of extracted vulcanizate, wt.-%	Wt. loss on extraction of raw vulcanizate, %	$[S_c + S^{2-}]$ of raw vulcanizate,[a] wt.-%	$[S^{2-}]$ of raw vulcanizate, wt.-%	$[S_c]$ $(\times 10^4)$[b]	$[S^{2-}]$ $(\times 10^{-4})$[c]	$(2M_{c,\mathrm{chem}}^{\mathrm{RH}})^{-1}$ $(\times 10^4)$[d]	E[e]	F[f]
Mix A: hr. at 100°C.									
3	0.25	14.4	0.18₅	0.026	0.61	0.10	0.10	6.1	1.0
8	0.55	13.7	0.45	0.069	1.44	0.26	0.36	4.0	0.73
10	0.72	12.7	0.61	0.132	1.79	0.50	0.47	3.8	1.1
16	—	—	—	0.198	—	0.75	0.57	—	1.3
24	1.13	13.4	0.96	0.304	2.46	1.15	0.80	3.1	1.4
48	1.41	12.6	1.21	0.427	2.96	1.62	1.09	2.7	1.5
144	1.52	11.5	1.32	0.563	2.88	2.13	1.20	2.4	1.8
336	1.55	14.1	1.30	0.623	2.58	2.36	0.93	2.8	2.5
Mix B: min. at 140°C.									
10	0.37	14.2	0.29	0.037	0.95	0.14	0.16	6.0	0.9
15	0.59	13.4	0.48	0.075	1.53	0.28	0.25	6.1	1.1
30	0.94	13.1	0.79	0.205	2.20	0.78	0.44	5.0	1.8
60	1.19	13.1	1.01	0.310	2.65	1.17	0.57	4.6	2.1
90	1.41	11.8	1.22	0.437	2.94	1.66	0.70	4.2	2.4
120	1.50	12.4	1.28	0.485	2.99	1.84	0.70	4.3	2.6
240	1.57	13.0	1.34	0.593	2.84	2.25	0.71	4.0	3.1
360	1.56	12.2	1.34	0.609	2.77	2.31	0.67	4.1	3.5
480	1.60	12.0	1.38	0.623	2.88	2.36	0.69	4.2	3.4

Mix E: S (pphr.) 144 hr. at 100°C.

			g					
0.4	0.50	13.8	0.40	0.139	0.98	0.53	0.34	2.9	1.6
0.5	0.62	13.5	0.51	0.176	1.25	0.67	0.42	3.0	1.6
0.6	0.67	12.9	0.55	0.216	1.26	0.82	0.50	2.5	1.7

Mix E: S (pphr.) 336 hr. at 100°C.

0.3	0.41	13.7	0.33	0.122	0.77	0.46	0.24	3.2	1.9
0.5	0.60	13.8	0.49	0.218	1.02	0.82	0.35	2.9	2.4
0.8	0.94	13.2	0.79	0.351	1.64	1.33	0.54	3.0	2.5
1.1	1.24	12.5	1.10	0.425	2.39	1.61	0.70	3.4	2.3

[a] Corrected for the sulfur content of the raw rubber.
[b] Gram-atom sulfur per gram rubber hydrocarbon in the network.
[c] Gram-ion sulfide per gram rubber hydrocarbon in the network.
[d] Gram-mole chemical crosslinks per gram rubber hydrocarbon in the network.
[e] Number of sulfur atoms combined in the network per chemical crosslink present.
[f] Number of sulfide ions formed per chemical crosslink present in the network.
[g] Determined on 1 g. samples of the unextracted vulcanizates milled (2 passes at room temperature) to sheets 0.1–0.2 mm. thick and then treated with a mixture of acetic acid, hydrochloric acid, and water (5:1:1 by vol.); hydrogen sulfide was determined as before.

where R is a rubber chain and $x \geq 1$.   Modifications not containing sulfur, such as conjugated diene and triene groups, are also formed.

By contrast, the E value for system A, initially about 6, decreases with reaction time to the very low value of 2.4.   This very efficient vulcanizing system evidently produces a relatively simple network structure, which becomes still more simple on further reaction.   In this case treatment with triphenylphosphine showed that relatively little of the combined sulfur is present as main-chain modifications.[22,24]   A further striking difference between systems A and D, one which is indicative of the chemical processes
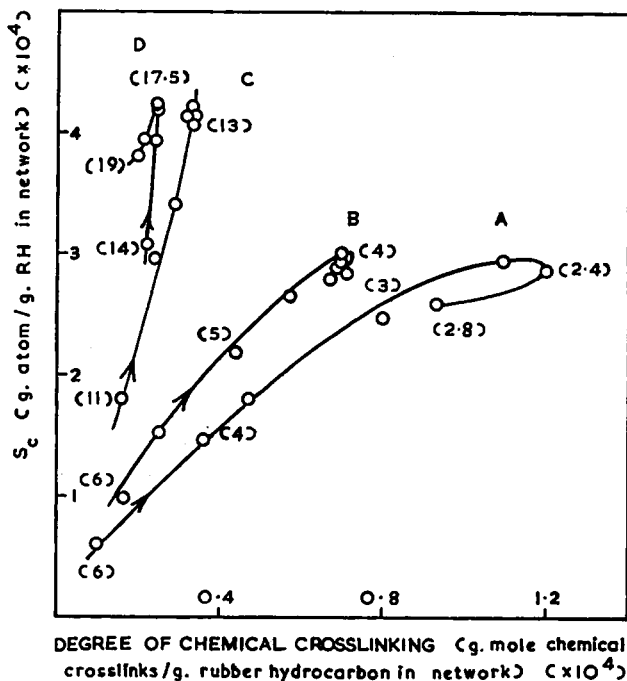
Fig. 4. Relationship between sulfur combined in the network, S_c, and degree of chemical crosslinking, $(2M_{c,\,chem}^{RH})^{-1}$ as a function of mix formulation (mixes A–D) and vulcanization conditions (Table II).   Arrows on curves indicate direction of increasing vulcanization time. Values of the sulfur crosslinking efficiency E are given in parentheses on the curves.

taking place, lies in their behavior after most of the sulfur has been combined; whereas with system D there is a slight loss of sulfur from the network, accompanied by an appreciable loss of crosslinks, a similar loss of sulfur from the networks prepared from system A is accompanied by the insertion of more crosslinks.   In the latter case sulfur already combined in the network (in forms now recognized as polysulfidic crosslinks and polysulfidic pendent groups[11,22,24,26]) can evidently give rise to new crosslinks by further reaction, whereas similarly combined sulfur in the crosslinks from system D is less effective in this role.

The contrasting behavior of systems A and D may be rationalized in terms of the subsequent reactions of the initially formed crosslinks, which are polysulfidic in nature.[11,22,24] Such crosslinks are subject to two competing reactions: (1) they may be progressively desulfurated by a complex formed from the zinc mercaptide of the accelerator (i.e., ZMBT) and the zinc laurate to give, eventually, monosulfidic crosslinks, the sulfur removed from the crosslinks being reused to form additional crosslinks, or (2) they may undergo thermal decomposition with the formation of cyclic monosulfide and conjugated diene and triene groups along the rubber chains. The relative rates of these two reactions control the changes in the number and nature of the crosslinks with time and the structure of the final vulcanizate network. Thus, if reaction (1) predominates, the sulfur chain length in the crosslinks is rapidly reduced to 1, the reutilization of the sulfur leads to more crosslinks, and very little modification of the main rubber chains by cyclic monosulfide or conjugated diene or triene groups takes place. This results finally in a very simple, efficiently crosslinked network, whose crosslinks are monosulfidic and therefore stable to further heat treatment. If reaction (2) predominates, the crosslinks remain largely polysulfidic and decompose thermally, leading ultimately to complex networks containing relatively few crosslinks but a large number of main-chain modifications.

The predominance of reaction (1) in system A is demonstrated by the low E values attained after long reaction times, the small proportions of sulfur removed from the networks by triphenylphosphine[22,24] and the small proportion of crosslinks cleaved by sodium di-n-butyl phosphite in benzene[22,24] (which breaks di- and polysulfidic crosslinks) at the same stage of reaction, and the formation of mono- and disulfides only, when 2-methyl-2-pentene is heated with a similar reaction system for 336 hr. at 100°C.[27] The rubber networks produced by mix A (and to a lesser extent by mix B) after extensive reaction are thus efficiently vulcanized networks.[28]

Similar types of evidence show that in system D reaction (2) predominates over reaction (1). Thus, E values are high and increase with reaction time, while much of the combined sulfur is inert towards triphenylphosphine,[22,24] the majority of the crosslinks are cleaved by sodium di-n-butyl phosphite even after long reaction times,[22,24] and methylpentenyl *polysulfides* are the major reaction products of treatment of 2-methyl-2-pentene with a similar reaction system for 2 hr. at 140°C.[27]

The differences between systems A and B and between systems C and D are probably due to a larger increase in the rate of reaction (2) with temperature compared with reaction (1). In each case use of the higher vulcanization temperature leads to a reduction in the maximum number of crosslinks formed from the given amount of sulfur, and E values increase, especially after long reaction times. These features are consistent with more rapid thermal breakdown of polysulfidic crosslinks as the vulcanization temperature is raised, with consequent redistribution of combined sulfur into main-chain modifications.

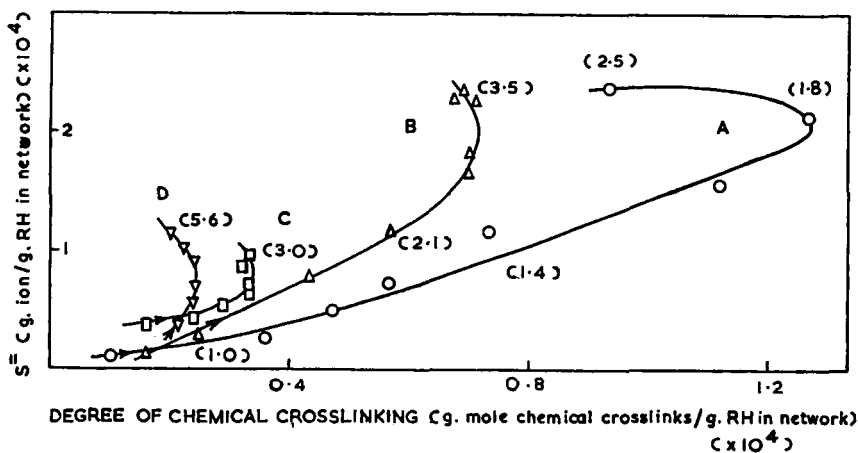The predominance of reaction (1) in systems A and B may be traced to

Fig. 5. Relationship between zinc sulfide sulfur, S^{2-}, formed and degree of chemical crosslinking $(2M_{c,\text{chem}}^{RH})^{-1}$ in the network as a function of mix formulation (mixes A–D) and vulcanization conditions (Table II). Arrows on curves indicate direction of increasing vulcanization time. Values of F, g.-ion of sulfide formed per chemical crosslink present in the network, are given in parentheses on the curves.

two main causes, both of which are related to the presence in the mixes of a large quantity of zinc laurate, which forms an active, soluble complex[1,29,30] with the potential accelerator, ZMBT, which is otherwise sparingly soluble and hence inactive. The dissolution in the rubber, as the zinc laurate complex, of all the available ZMBT increases the concentration of the agent which desulfurates polysulfides and hence increases the rate of reaction (1). Furthermore, complex formation alters the chemistry of the initial crosslinking process and hence alters the detailed structure at the termini of the initially formed polysulfidic crosslinks;[11,24] this in turn affects the reactivity of these crosslinks towards subsequent desulfuration.[11,24,26] In the case of ZMBT–zinc laurate complexes these structural changes lead to increased reactivity towards desulfuration, i.e. an increase in rate of reaction (1).

Although mixes C and D will form the same quantity of ZMBT as mixes A and B, much of it will remain insoluble in the rubber and thus be ineffective in both sulfuration and desulfuration reactions. These vulcanizing systems therefore behave similarly to systems containing a much lower concentration of added MBT (for the same concentration of lauric acid or zinc laurate), as Barton and Hart originally indicated.[1]
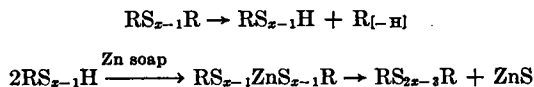
The features described above are also reflected in the yields of zinc sulfide relative to crosslinks as a function of the concentration of lauric acid in the mix and of the reaction temperature and reaction time (Fig. 5 and Tables VII and IX). Low yields of zinc sulfide per crosslink formed are associated with efficient use of sulfur for crosslinking purposes (see curve A of Fig. 5), while high yields of zinc sulfide per crosslink formed reveal inefficient use of sulfur as a crosslinking agent (see curve D of Fig. 5). It is sug-

gested that the zinc sulfide formed in excess of that required for the efficient crosslinking process,

$$2RH + -S_x- \xrightarrow{\text{ZnO}} RS_{x-1}R + ZnS + H_2O$$
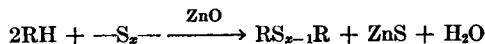
results from thermal destruction of initially formed polysulfide crosslinks and thus is indicative of network reversion processes:

$$RS_{x-1}R \rightarrow RS_{x-1}H + R_{[-H]}$$

$$2RS_{x-1}H \xrightarrow{\text{Zn soap}} RS_{x-1}ZnS_{x-1}R \rightarrow RS_{2x-3}R + ZnS$$

The small degree of main-chain modification present in efficiently vulcanized NR networks apparently controls their behavior towards swelling agents. The observed χ values in n-decane for selected networks from mix A (Table IV) are similar to those found[31] (0.411, std. dev. 0.008) for the simplest natural-rubber networks, viz. those obtained by vulcanization with an organic peroxide, in which the crosslinks contain no new atoms and in which other modifications are minimal.[11,24] Closely similar values have been found for other efficiently vulcanized networks.[32,33] The similarity of χ values for these networks to those for the carbon–carbon crosslinked networks, together with the lack of a marked trend in χ for the networks from mix A over the whole range of reaction times during which the crosslinks change from being almost entirely di- and polysulfidic to being about 55% monosulfidic,[22,24] indicates that the nature of the crosslinks has little influence on χ. However, changes in the network structure other than at the crosslinks have a notable effect on χ, as shown by the data for systems C and D (Table VI) and for other inefficient vulcanizing systems.[22,34] The introduction of main-chain modifications in the form of cyclic sulfide groups, conjugated diene and triene units, and even of *trans*-, rather than *cis*-, trialkylethylenic double bonds,[35] appears to raise the χ value (up to 0.54 for unaccelerated NR–sulfur networks in n-decane).[36]

References

1. B. C. Barton and E. J. Hart, *Ind. Eng. Chem.*, **44**, 2444 (1952).
2. O. Lorenz and E. Echte, *Kautschuk Gummi*, **10**, WT81 (1957).
3. W. Scheele, *Rubber Chem. Technol.*, **34**, 1306 (1961).
4. W. Scheele and K.-H. Hillmer, *Kautschuk Gummi*, **16**, 655 (1963).
5. B. C. Barton, *J. Polymer Sci.*, **18**, 559 (1955).
6. L. Mullins, *J. Polymer Sci.*, **19**, 225 (1956).
7. L. Mullins, *J. Appl. Polymer Sci.*, **2**, 1 (1959).
8. C. G. Moore and W. F. Watson, *J. Polymer Sci.*, **19**, 237 (1956).
9. G. M. Bristow and M. Porter, *J. Appl. Polymer Sci.*, **11**, 2215 (1967): Part V of the series.
10. C. G. Moore and M. Porter, *Rev. Gén. Caoutchouc*, **39**, 1768 (1962).

11. L. Bateman, Ed., *The Chemistry and Physics of Rubber-like Substances*, Maclaren, London, 1963, Chap. 15.

12. C. G. Moore and A. A. Watson, *J. Appl. Polymer Sci.*, **8**, 581 (1964): Part III of the series.

13. C. G. Moore, L. Mullins, and P. McL. Swift, *J. Appl. Polymer Sci.*, **5**, 293 (1961): Part I of the series.

14. *British Standard 1673*, Pt. 2, Sect. 2.3 (1954).

15. L. Mullins and W. F. Watson, *J. Appl. Polymer Sci.*, **1**, 245 (1959).

16. *British Standard 903*, Pt. 3, Sect. 3.5 (1950).

17. W. J. Dermody, private communication.

18. *British Standard 1673*, Pt. 4, Sect. 4.62 (1953).

19. *British Standard 903*, Pt. A2 (1956).

20. L. Mullins and D. T. Turner, *J. Polymer Sci.*, **43**, 35 (1960).

21. H. W. Greensmith and D. O'Dwyer, unpublished work.

22. C. G. Moore and B. R. Trego, *J. Appl. Polymer Sci.*, **8**, 1957 (1964): Part IV of the series.

23. L. Bateman, Ed., *The Chemistry and Physics of Rubber-like Substances*, Maclaren, London, 1963, Chap. 19.

24. C. G. Moore, in L. Mullins, Ed., *Proceedings of the Natural Rubber Producers' Research Association Jubilee Conference, Cambridge, 1964*, Maclaren, London, 1965.

25. G. M. C. Higgins, M. Porter, and B. K. Tidd, unpublished work.

26. A. A. Watson, unpublished work.

27. M. Porter, Ph.D. Thesis, London University, 1964.

28. T. D. Skinner and A. A. Watson, *Rubber Age*, in press.

29. A. Y. Coran, *Rubber Chem. Technol.*, **36**, 679 (1964).

30. B. Milligan, *Rubber Chem. Technol.*, **39**, 1115 (1966).

31. G. M. Bristow, *J. Appl. Polymer Sci.*, **9**, 1571 (1965).

32. M. Porter, *J. Appl. Polymer Sci.*, **11**, 2255 (1967): Part VII of the series.

33. M. Porter, *Rubber Chem. Technol.*, **40**, 866 (1967).

34. M. Porter, T. D. Skinner, and M. A. Wheelans, *J. Appl. Polymer Sci.*, **11**, 2271 (1967): Part VIII of the series.

35. D. J. Elliott and C. G. Moore, *J. Appl. Polymer Sci.*, **11**, 2285 (1967): Part IX of the series.

36. G. M. Bristow, unpublished work.

Résumé

L'efficacité de pontage du soufre dans la vulcanisation du caoutchouc naturel en présence de 2-mercaptobenzothiazole, d'oxyde de zinc et d'acide laurique a été déterminée en fonction de la durée du traitement, de la température et de la concentration en acide laurique. A une concentration faible en acide laurique, il se formait des réseaux de structure complexe qui contiennent de 11 à 19 atomes de soufre combiné par pont chimique présent. La complexité croît avec la durée de la vulcanisation. A concentration élevée en acide laurique, des réseaux beaucoup plus simples sont formés qui deviennent progressivement plus simples à mesure que la réaction progresse (6 atomes de soufre combiné dans le réseau par pontage chimique décroissant jusque 2.4 avec le temps). En augmentant la température de traitement de 100 à 140°C, l'efficacité de pontage est diminuée dans les deux cas. Les variations d'efficacité sont attribuées à l'influence des variables de la réaction en particulier, la concentration de complexes solubles—caoutchouc du laurate de zinc avec le mercaptide de benzothiazolyl zinc—sur la structure et les réactions subséquentes des ponts polysulfures initialement formés.

Zusammenfassung

Die Vernetzungswirksamkeit von Schwefel bei der Vulkanisation von Naturkautschuk in Gegenwart von 2-Mercaptobenzothiazol, Zinkoxyd und Laurinsäure wurde als Funktion von Vulkanisationsdauer, Vulkanisationstemperatur und Laurinsäurekonzentration

bestimmt. Mit niedriger Laurinsäurekonzentration werden strukturell komplexe Netzwerke gebildet, welche 11–19 gebundene Schwefelatome pro vorhandener chemischer Vernetzung enthalten. Der komplexe Charakter nimmt mit der Vulkanisationsdauer zu. Bei hoher Laurinsäurekonzentration bilden sich viel einfachere Netzwerke, die mit fortschreitender Reaktion immer einfacher werden (6 im Netzwerk gebundene Schwefelatome pro chemischer Vernetzung nehmen mit steigender Reaktionsdauer auf 2,4 ab). Steigerung der Vulkanisationstemperatur von 100° auf 140°C verringert in beiden Fällen die Vernetzungsausbeute. Die Ausbeuteänderungen werden auf den Einfluss der Reaktionsvariablen—im besonderen der Konzentration der kautschuklöslichen Zinklaurat–Zinkbenzothiazolmercaptid-Komplexe—auf die Struktur und die Reaktionen der anfänglich gebildeten Polysulfidvernetzungen zurückgeführt.