THE STRUCTURE OF ACCELERATED SULPHUR VULCANIZATES
OF
STYRENE-BUTADIENE RUBBER
AND
ACRYLONITRILE-BUTADIENE RUBBER

by

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ABSTRACT

Structural characterisation of CBS-accelerated vulcanizates of SBR and NBR as a function of type of cure system and cure time was investigated. It was found that SBR and NBR vulcanizates obtained from cure systems with accelerator to sulphur (A/S) ratio of 0.6/2.5 have higher crosslink densities than that obtained from A/S ratio of 1/2. SBR and NBR vulcanizates were found to exhibit modulus reversion on prolonged curing. For the same cure system, SBR vulcanizates were found to show greater degree of modulus reversion than the NBR vulcanizates and the degree of modulus reversion in both rubbers increased with decrease in A/S ratio. As expected, the proportion of monosulphidic crosslinks increased at the expense of poly- and disulphidic crosslinks with increasing cure time although dissimilarities in detail behaviour were observed. The crosslinking efficiency for both cure systems used were relatively low. The crosslinking efficiency parameter, E, was observed to decrease for NBR but the E value for SBR vulcanizates exhibited different tendencies. The amount of main chain modifications occuring was found to increase on prolonged curing and this increase was much greater in vulcanizates obtained from A/S ratio of 0.6/2.5.

The polymer-benzene interaction parameter, χ, was observed to vary with cure systems and cure time. Chemical

probe treatments had the effect of reducing the χ value.

ABSTRAK

Pencirian struktur vulkanisat SBR dan NBR yang dipecutkan oleh CBS sebagai fungsi sistem-sistem pematangan dan masa pematangan akan diselidiki. Vulkanisat SBR dan NBR dari sistem pematangan dengan nisbah pemecut kepada sulfur (A/S) 0.6/2.5 didapati mempunyai ketumpatan sambung-silang yang lebih tinggi dari sistem pematangan dengan nisbah (A/S) 1/2. Pematangan yang berlanjutan terhadap vulkanisat SBR dan NBR menunjukkan penerbalikan modulus. Untuk sistem pematangan yang sama, vulkanisat SBR menunjukkan penerbalikan modulus yang lebih tinggi daripada vulkanisat NBR dan darjah penerbalikan modulus bagi kedua-dua getah bertambah dengan pengurangan nisbah A/S. Seperti yang dijangkakan, kadaran sambung-silang monosulfida bertambah dan kadaran sambung-silang poli- dan disulfida berkurangan dengan pertambahan dalam masa pematangan walaupun terdapat ketaksamaan dalam kelakuan detil. Secara relatif kecekapan sambung-silang bagi kedua-dua sistem pematangan yang diselidiki didapati rendah. Parameter kecekapan sambung-silang, E, didapati berkurang untuk NBR tetapi nilai E untuk vulkanisat SBR menunjukkan kecenderungan yang berlainan. Pengubahsuaian rantai utama didapati bertambah dengan pematangan yang berlanjutan dan pertambahannya adalah lebih tinggi dalam vulkanisat yang bernisbah (A/S) 0.6/2.5.

Parameter saling-tindakan polimer-benzena, χ, didapati

berubah dengan sistem pematangan dan masa pematangan. Pengolahan bahan kimia ujiselidik terhadap vulkanisat mengurangkan nilai χ .

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LIST OF ABBREVIATIONS

A/S	Accelerator to sulphur
BR	High cis-1,4-polybutadiene rubber
CV	Conventional vulcanizing
CBS	N-cyclohexylbenzothiazole-2-sulphenamide
EV	Efficient vulcanizing
MRPRA	Malaysian Rubber Producers' Research Association
MBT	2-Mercaptobenzothiazole
NR	Natural rubber
NBR	Nitrile rubber
pphr	Part per hundred parts of rubber
S	Sulphur
SBR	Styrene-butadiene rubber
SEV	Semi-efficient vulcanizing
S_{Ni}	Internal allylic substitution reaction without rearrangement
S'_{Ni}	Internal allylic substitution reaction with rearrangement

1.1 Vulcanization

Raw rubber is a tough resilient material at room temperature but when placed under stress it undergoes plastic or irrecoverable flow, especially at high temperatures. By introducing a relatively small number of chemical crosslinks between individual polymer chains, the plastic flow of the rubber is overcome while the elastic recovery of the material is unimpaired. The insertion of these chemical crosslinks is known as vulcanization. This process results in several fundamental changes in the physical properties of the rubber. In particular, the rubber becomes insoluble in normal solvents like heptane, toluene, benzene and chloroform; instead, it swells, often considerably but to an equilibrium volume. Also, the load-bearing characteristic improves since the crosslinks introduced prevent viscous flow of the rubber chains. The crosslinks produced may be chains of sulphur atoms, single sulphur atom, carbon-carbon bonds, polycovalent organic radicals, or polycovalent metal ions.

There are various ways to crosslink rubbers, namely using elemental sulphur, sulphur donors, organic peroxides, phenolic resins, metal oxides, and high energy radiation. These methods have already been extensively reviewed by Elliot & Tidd(1974) and Kirkham(1973). The choice of method depends on the properties required by the end product for a particular application. Since accelerated sulphur vulcanization was used in this project, it will be discussed in detail here.

1.2 Accelerated Sulphur Vulcanization

Accelerated sulphur vulcanization, which had its origin in the well known discoveries of Goodyear and Hancock, is still the most widely used crosslinking method today. This method is suitable for the following rubbers : natural rubber (NR), synthetic isoprene rubber, polybutadiene (BR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), butyl rubber, chloroprene, and ethylene-propylene-diene modified rubber. The process of vulcanization involves the blending of masticated raw rubber with a vulcanizing system consisting of a pre-formulated mixture of vulcanizing agents, accelerators, and activators. Vulcanization is effected by curing the mix in a mould under pressure at a specified temperature and time. Heating is usually at 140°C for NR and somewhat higher for SBR and NBR (up to 150-160°C); much lower temperatures are possible if specially active accelerators are used.

1.2.1 Sulphur vulcanizing system

A vulcanizing system is a mixture of additives required to vulcanize an elastomer. The system generally employed for curing rubber goods consists of three main classes of chemicals, namely vulcanizing agents, accelerators, and activators.

(a) Vulcanizing agents

A vulcanizing agent is any chemical which can initiate the chemical crosslinking of the rubber molecules leading to the formation of a three-dimensional network. The most common vulcanizing agent used is sulphur.

(b) Accelerators

As the name implies, these are substances which can increase the rate of vulcanization of rubber with sulphur. They are also capable of promoting more efficient utilization of sulphur for crosslinking, thereby improving the properties of the vulcanizates. Most of these are organo-nitrogen or organo-sulphur compounds like amines, guanilines, thioureas, thiazoles, sulphenamides, thiurams, dithiocarbamates, and xanthates.

(c) Activators

These are used to increase the vulcanization rate by activating the accelerator so that it becomes more efficient. Activators can be grouped as follows :

(1) Inorganic compounds (mainly metal oxides) such as

zinc oxide, hydrated lime, litharge, red lead, magnesium oxide, and alkali carbonates. Zinc oxide is the most commonly used inorganic activator.

(2) Organic carboxylic acids which are normally used in combination with metal oxides. They are generally high molecular weight monobasic acids such as stearic, oleic, lauric, palmitic, and myristic acids.

Apart from the above, there are other compounding ingredients, present mostly in industrial rubber compounds, such as fillers, reinforcing agents, antidegradants, retarders, and softeners.

Generally, the vulcanizing systems used in the vulcanization of NR can be divided into three different types based on the ratio of accelerator concentration to sulphur concentration (A/S ratio) as shown in Table 1.1.

Table 1.1 Sulphur and accelerator concentrations for different vulcanizing systems (Elliot & Tidd, 1974)

Systems	Sulphur (pphr)*	Accelerator (pphr)*
Conventional	2.0 to 3.5	1.0 to 0.4
Efficient	0.3 to 0.8	6.0 to 2.5
Semi-efficient	1.0 to 1.7	2.5 to 1.0

*pphr - part per hundred parts of rubber

Conventional vulcanizing (CV) systems

The A/S ratio is low in these systems. At optimum cure, the crosslinks are predominantly poly- and disulphidic with a small number of monosulphidic crosslinks. At the same time, much of the sulphur is combined with rubber molecules in the intramolecular cyclic groups and pendent groups and hence wasted as far as crosslinking is concerned. A typical example of CV systems that had been studied in detail is as follows(Moore, 1964) : sulphur=2.5, CBS=0.6, zinc oxide=5.0, fatty acid=0.7 (all pphr).

Efficient vulcanizing (EV) systems

These systems have high A/S ratios. At optimum cure the crosslinks are mainly monosulphidic with little di- and polysulphidic types. The amounts of cyclic and pendent groups in EV systems are relatively small compared with those present in CV systems. A typical example of EV systems that had been studied in detail is as follows(Moore, 1964) : sulphur=0.4, CBS=6.0, zinc oxide=5.0, fatty acid=1.0 (all pphr).

Semi-efficient vulcanizing (SEV) systems

These systems produce vulcanizates whose network structures and thermal stability are intermediate to those from CV amd EV systems. It can be used in cases where it can offer a compromise, in terms of cost and certain properties, between CV and EV systems. A typical example of

SEV systems that had been studied in detail is as follows (Skinner, 1972) : sulphur=1.8, CBS=1.0, zinc oxide=5.0, fatty acid=1.4 (all pphr).

It should be noted that Table 1.1 is a very simplified presentation. In practice the amount of accelerator required to obtain an optimum degree of crosslinking for any given sulphur level, will depend on several factors such as the activity of the accelerator, the presence of inorganic and/or organic activator(s), and whether just one or a combination of two or more accelerators is used.

The terms CV, EV, and SEV are similarly applicable to describe the vulcanizing systems used in the vulcanization of synthetic rubbers. However, as shown by Rodger (1979), the A/S ratio used in CV systems for any synthetic rubbers is generally higher than that used in NR.

1.2.2 Chemical structure of accelerated sulphur vulcanizate

As a result of chemical reactions that take place during vulcanization, the primary rubber molecules of NR are converted into a three-dimensional covalently bonded vulcanizate network having the structural features as illustrated in Fig. 1.1. The network itself consists of :

(a) the main chain of original rubber molecules

(b) crosslinks with variations defined by knowledge of both actual atom interlinking main chains and

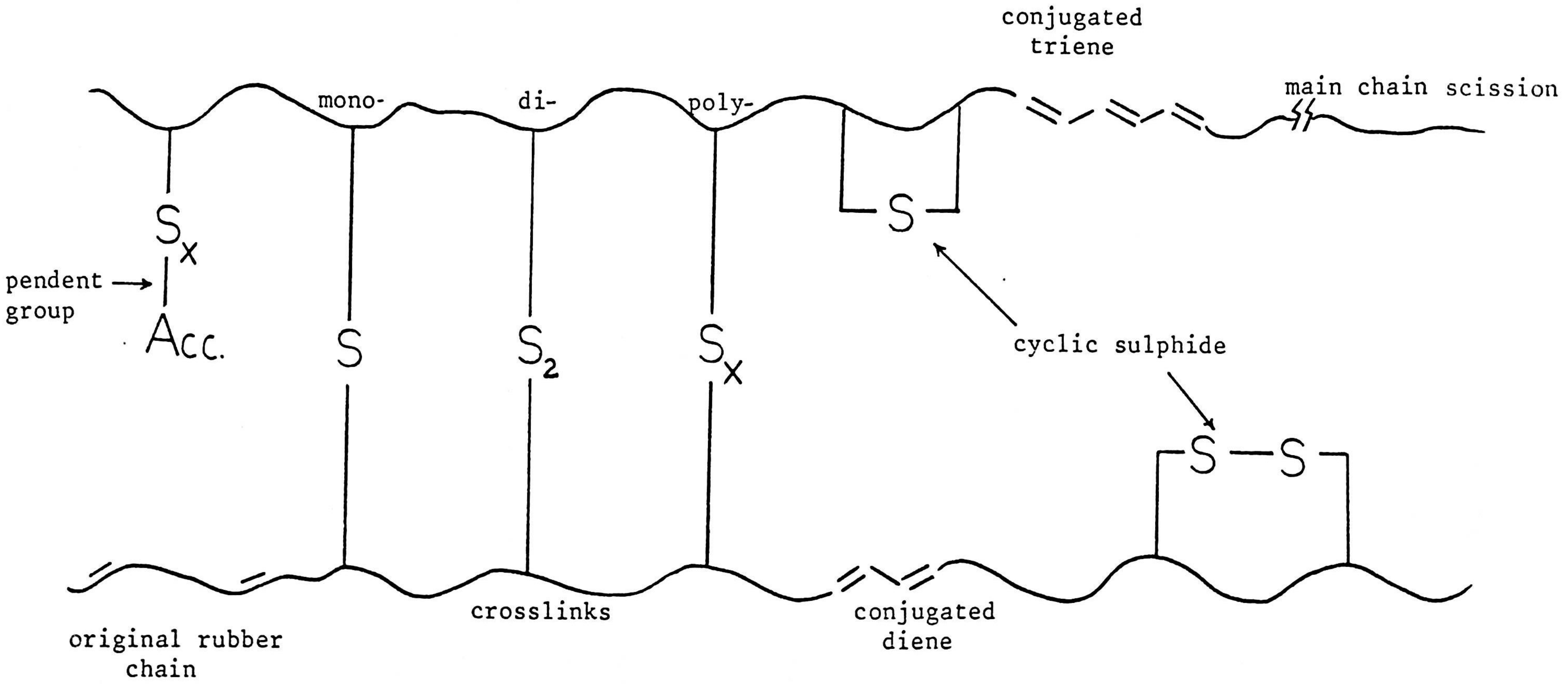


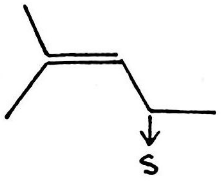
Fig. 1.1: General features of sulphur vulcanizates of NR (Moore, 1964).

immediate vicinity of the crosslink.

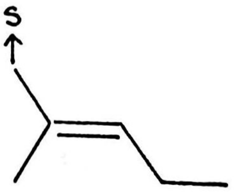
(c) chemical modifications of the main chain, for example cyclic sulphides, pendent sulphur/accelerator fragments, olefinic pattern changes in parent molecules (diene and triene), and main chain scission.

Not all groupings of the above structures are present in every case. Relative concentrations of each may vary widely depending particularly on the molar accelerator to sulphur used, activator concentrations, time and temperature of vulcanization.

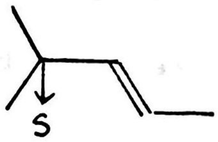
The covalent sulphide linkages produced join together neighbouring rubber chains at randomly selected points along each primary molecule. The points of attachment of the sulphide linkages to the molecular chain depend on the nature of the chain. Model system studies by Porter (1968) have shown that the point of attachment is either at carbon atoms α-methylic or α-methylenic to the double bond as shown below :



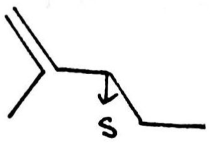
(A_1S-)



(B_1S-)



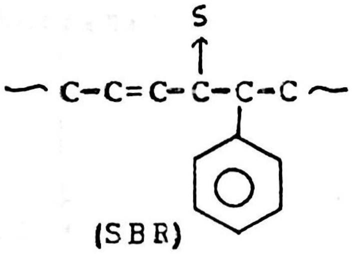
(A_2S-)



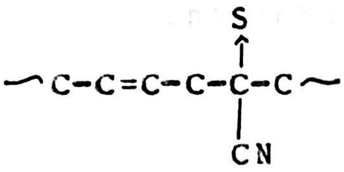
(B_2S-)

The terminal alkenyl groups are designated A_1 or B_1 and their allylic-isomeric forms A_2 or B_2 according to their point of attachment of olefin to sulphur.

In contrast to the amount of information concerning the structure of NR vulcanizates, there is very little information available on synthetic rubbers. Limited studies by Brour & Vorohkov (1947) for SBR, Zakharov & Kostrykina(1968), and Zakharov et al.(1971) for NBR have suggested that the point of attachment for the sulphidic linkages occurs at the carbon atom α-methylenic to the double bond and phenyl ring, and at the carbon atom adjacent to the nitrile group for SBR and NBR respectively as shown below :



(SBR)



(NBR)

1.2.3 Mechanism of accelerated sulphur vulcanization

Vulcanization of NR with sulphur in the presence of accelerators is believed to follow the reaction sequence represented in Fig. 1.2.

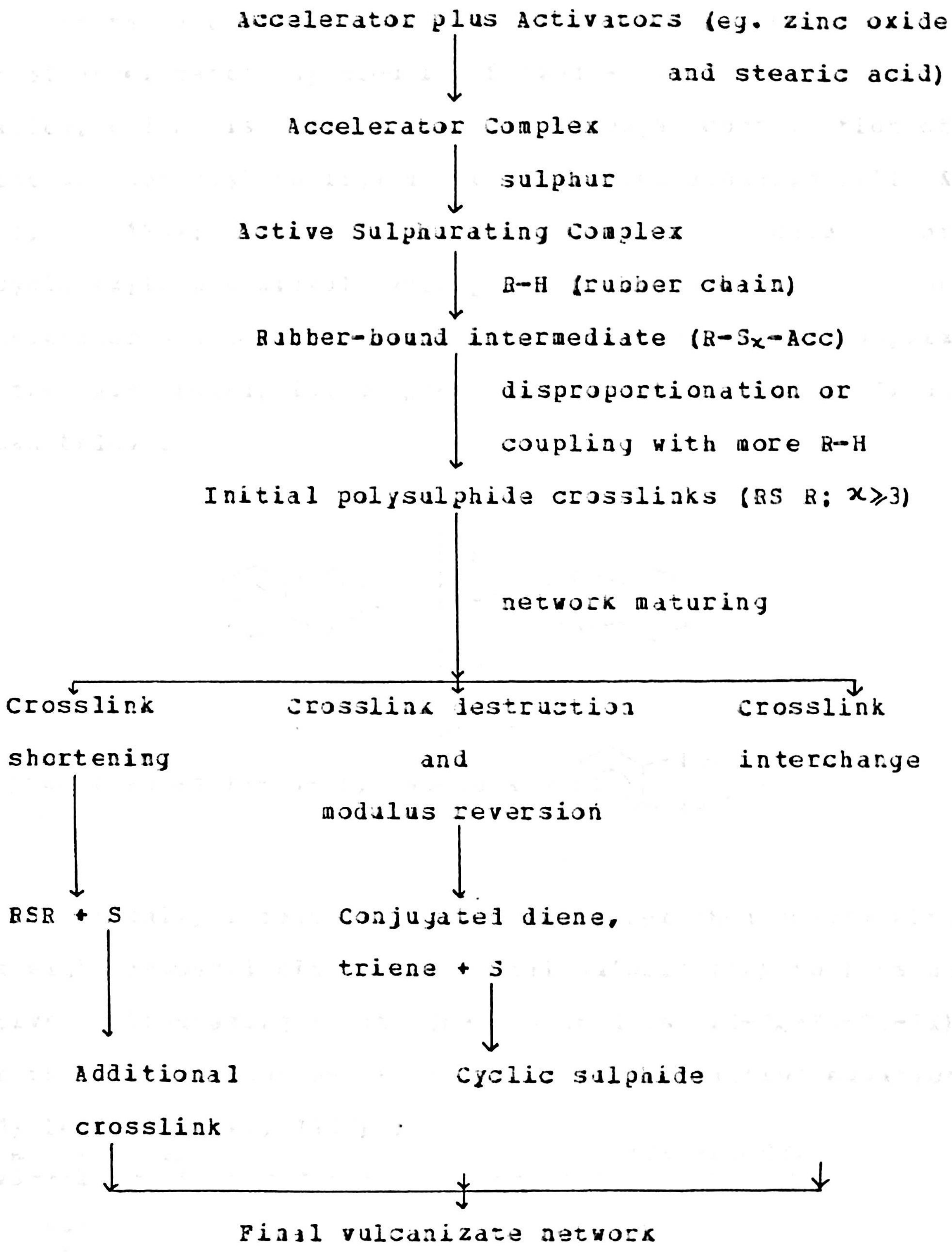
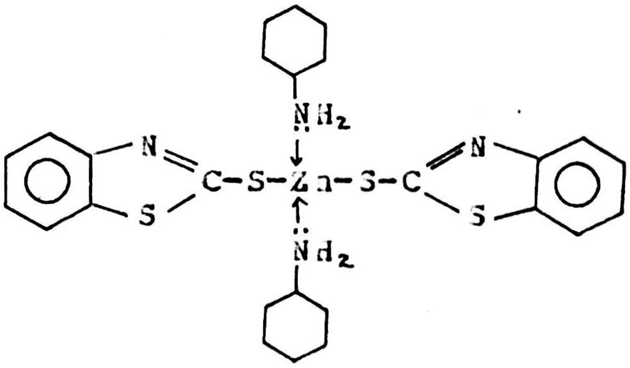
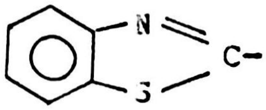


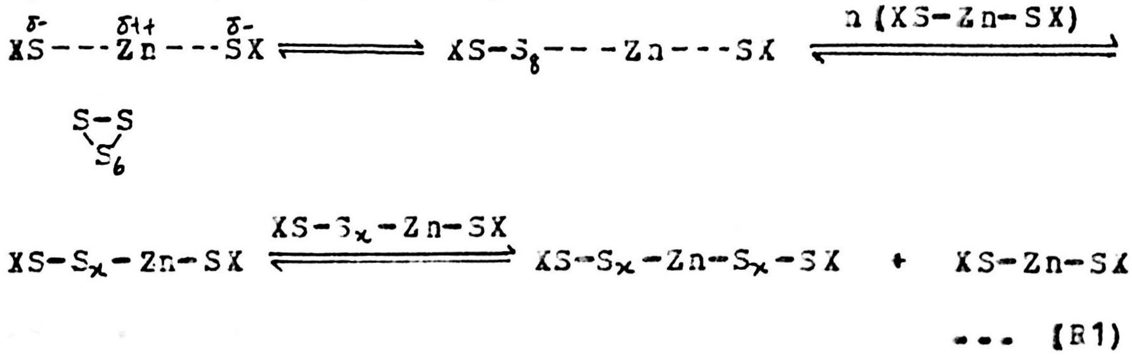
Fig. 1.2 The course of the overall vulcanization process (Moore, 1964)

In the early stage of the vulcanization process, the actual accelerator species is formed - a zinc/accelerator complex, which is rendered soluble through coordination of amine or carboxylate ligands to the zinc atom(Campbell & Wise, 1964; 1971). In the case of N-cyclohexylbenzothiazole-2-sulphenamide (CBS), the accelerator species is possibly the cyclohexylamine complex of the zinc mercaptide of 2-mercaptobenzothiazole (MBT) as shown below :



represented as XS-Zn-SX, where X = 

It is generally recognised that the complex then reacts with the eight-membered ring of elemental sulphur (S_8) to form an active sulphurating agent (represented as XS-S_x-Zn-S_x-SX) for the NR hydrocarbon as shown in the reaction equation (R1) below (Porter, 1968) :



$$\underset{\substack{S-S\\ S_6}}{\overset{\delta-}{XS}---\overset{\delta++}{Zn}---\overset{\delta-}{SX}} \rightleftharpoons XS-S_8---Zn---SX \xrightleftharpoons{n(XS-Zn-SX)}$$

$$XS-S_x-Zn-SX \xrightleftharpoons{XS-S_x-Zn-SX} XS-S_x-Zn-S_x-SX + XS-Zn-SX$$

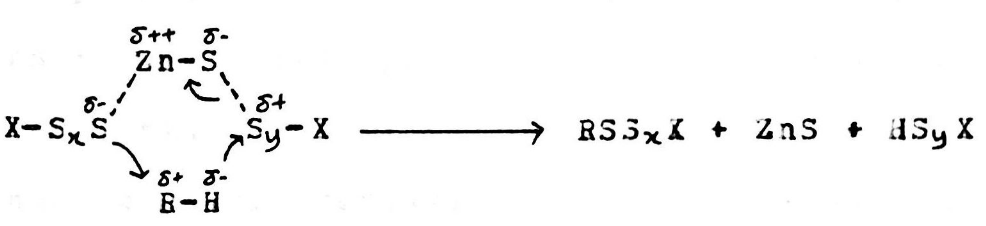
... (R1)

Thus the activator serves two important functions :

(1) it increases the solubility of the accelerator in the rubber hydrocarbon and

(2) it increases the polarization of the Zn---S bond in the accelerator complex and thus the nucleophilic reactivity of incipient mercaptide ion with the S-S bond in the S_8 ring and hence facilitates the production of the active sulphurating agent.

The active sulphurating agent then reacts with the rubber hydrocarbon (represented as R-H) to form polysulphidic pendent groups (represented as $R-S-S_x-X$), which are believed to be the intermediate precursors of polysulphidic crosslinks. The proposed mechanism involves nucleophilic attack by terminal persulphenyl anions in the sulphurating complex on α- carbon atom; this is accompanied by the simultaneous displacement of hydride ions towards penultimate persulphenyl cations and formation of zinc sulphide as illustrated in reaction equation R2 below (Bateman *et al.*, 1953b) :

 ... (R2)

Substitution takes place either at α-methylic or α-methylenic carbon atoms according to factors such as electronic character of the sulphuration complex, the steric accessibility of α-carbon atom and the polarizability of C-H bonds.

In contrast to NR, information on the mechanism of vulcanization of SBR and NBR are limited. For SBR, Ghosh et al.(1977) proposed that sulphuration proceeds through a polar mechanism and the reaction site is at the carbon atom α-methylenic to the double bond and phenyl ring. However, for NBR, Zakharov & Kostrykina(1968) and Zakharov et al.(1971) found that the mechanism of sulphuration is via a radical reaction with the participation of the $-\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H}$ group adjacent to the nitrile group.

In the vulcanization of NR, the initial crosslinks are thought to be formed either by disproportionation between pendent groups on neighbouring chains or by direct reaction of pendent intermediate groups with rubber hydrocarbon. The fate of the initial polysulphidic crosslinks has been revealed by experiments with model dialkenyl di- and trisulphides(Porter, 1968). It was found that the initial polysulphide crosslinks formed can undergo any of the competitive routes as shown in Fig. 1.2. One of these routes is polysulphide crosslink shortening which can occur repetitively until the eventual formation of stable monosulphidic crosslinks. This releases sulphur for further crosslinking.

Alternatively, the polysulphide crosslinks may suffer destruction, resulting in main chain modifications. A third route is an interchange reaction occurring between polysulphide crosslinks at their point of attachment to the rubber chain which does not alter the crosslink composition of the network but leads to stress relaxation. These competitive routes together constitute the maturing process which controls the final structure of the vulcanizate network.

The predominance of any one of the maturing reactions depends on a number of factors. One of the important factors is the hydrocarbon structure of the group terminating the crosslink. Model system studies have shown that B_1 sulphides (see section 1.2.1) desulphurate faster than the A_1 sulphides. When the rate of desulphuration is high, there is little opportunity for thermal destruction of the initial polysulphide crosslinks and the associated formation of main chain modifications. Then the crosslink shortening reaction will dominate the maturing process and lead to the formation of additional crosslinks and a thermally stable network predominantly crosslinked by monosulphide. If, however, the rate of desulphuration is slow, the crosslinks will be retained in the polysulphide form for a longer period and hence become more susceptible to thermal destruction which will lead to modulus reversion and main chain modifications.

The maturing process will also be influenced by other factors :

(1) the structure and the concentration, and thus reactivity of the accelerator-activator complex which is responsible for the conversion of the elemental sulphur into the active sulphurating agent for the desulphuration of the polysulphide crosslinks.

(2) the length of the sulphur chain which is determined by the A/S ratio used; and

(3) the temperature and time of vulcanization.

1.3 Relationship between some Vulcanizates Properties and Network Structure

Fig. 1.3 illustrates some of the major effects of vulcanization. It can be seen that the modulus of a vulcanizate is substantially directly proportional to the number of crosslinks formed and hence the crosslink density. The relation between modulus and the degree of crosslinking is shown by the following equation (E1) :

$$f = \rho R T A_0 M_c^{-1} (\lambda - \lambda^{-2}) \quad \ldots \; (E1)$$

where f is the force applied, ρ is the density of the rubber network, A_0 is the area of unstrained cross-section of the test piece, R is the gas constant, T is the absolute temperature, M_c is the number average molecular weight of the network chains between physically effective crosslinks, and λ is the extension ratio. According to the equation, when ρ, T, A_o, and λ are kept constant, the force applied, f, at the extension ratio λ depends on the reciprocal of M_c and, therefore, on the degree of crosslinking.

Hardness of the vulcanizate, like modulus, increases progressively as the number of crosslinks increases until the material becomes ebonite. As is the case with modulus, a constant deformation (in this case, compression) is produced when hardness is measured. Therefore, what has been said about modulus also applies substantially to hardness.

Fig. 1.3 shows that tear strength and fatigue life increase with crosslink density until a maximum is reached after which these properties decrease with further increase in crosslink density. These properties are related to energy-at-break. Hysteresis and permanent set diminish as the degree of crosslinking increases. Since hysteresis is a measure of energy loss in a loading cycle, then those properties related to energy-at-break will increase with increase in crosslink density and hysteresis. However, hysteresis decreases as more crosslinks are formed. Therefore, the energy-at-break properties peak at some intermediate crosslink density.

Tensile strength does not increase continuously with the crosslink density (Fig. 1.3). Instead, it increases with the number of crosslinks until a maximum is reached, after which it falls with further crosslink formation. Qualitatively this can be explained from the fact that first an increase in strength wil be achieved as more network chains are to bear the stress. However, as vulcanization proceeds, the network chains become shorter and, therefore, less extensible and hence more prone to rupture before appreciable orientation of network as a whole occurs (Mullins, 1964).

The properties represented in Fig. 1.3 are not influenced by crosslink density alone but are also affected by the nature of crosslinks, the nature of base polymer, and the amount and type of filler used (if any). For example, when a given base polymer of a given initial molecular weight is crosslinked to the same extent by different vulcanizing systems, the resulting vulcanizates have varying tensile strength (Fig. 1.4). These differences are mainly because of the difference in the nature of crosslinks. Fig. 1.4 shows that CV systems give rubbers with higher tensile strength than rubbers cured with EV systems which, in turn, are stronger than peroxide or high energy radiation-cured rubbers. These three types of vulcanizates contain mainly polysulphidic, monosulphidic and carbon-carbon crosslinks respectively. Further, bond energy for rupture of the carbon-carbon, carbon-sulphur and sulphur-sulphur bond decreases in this order.

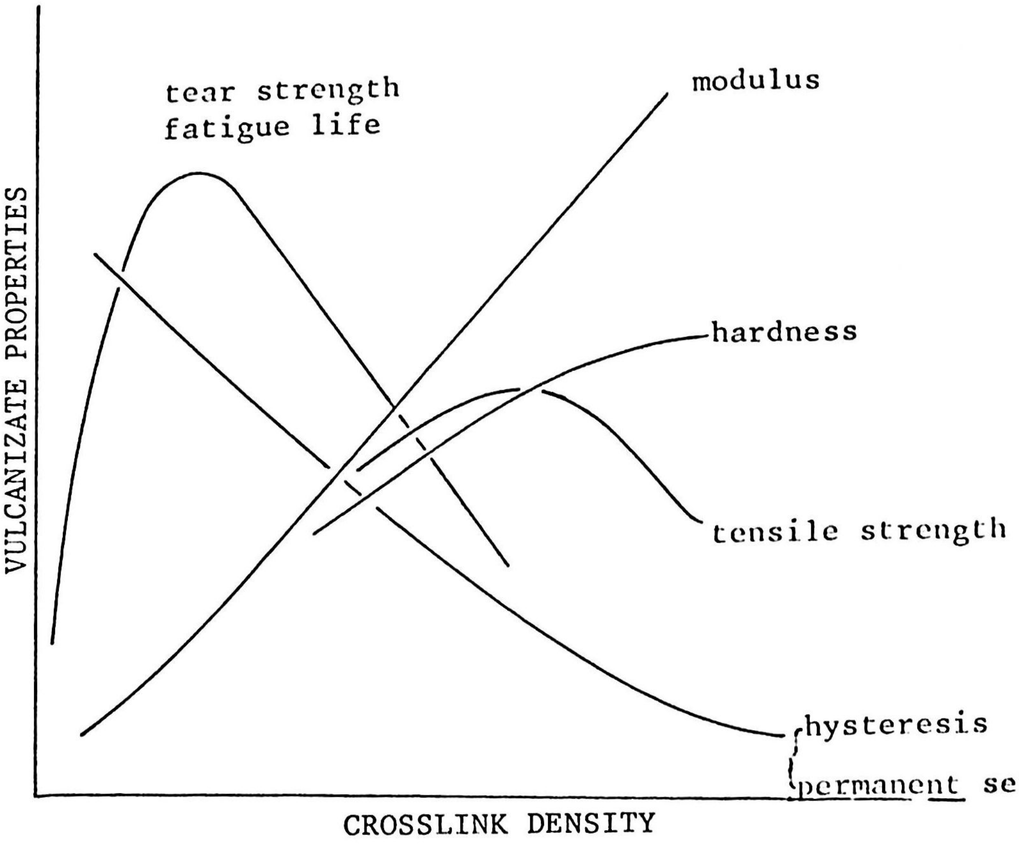


Fig. 1.3: Effect of crosslink density on various vulcanizate properties (Elrich, 1978).

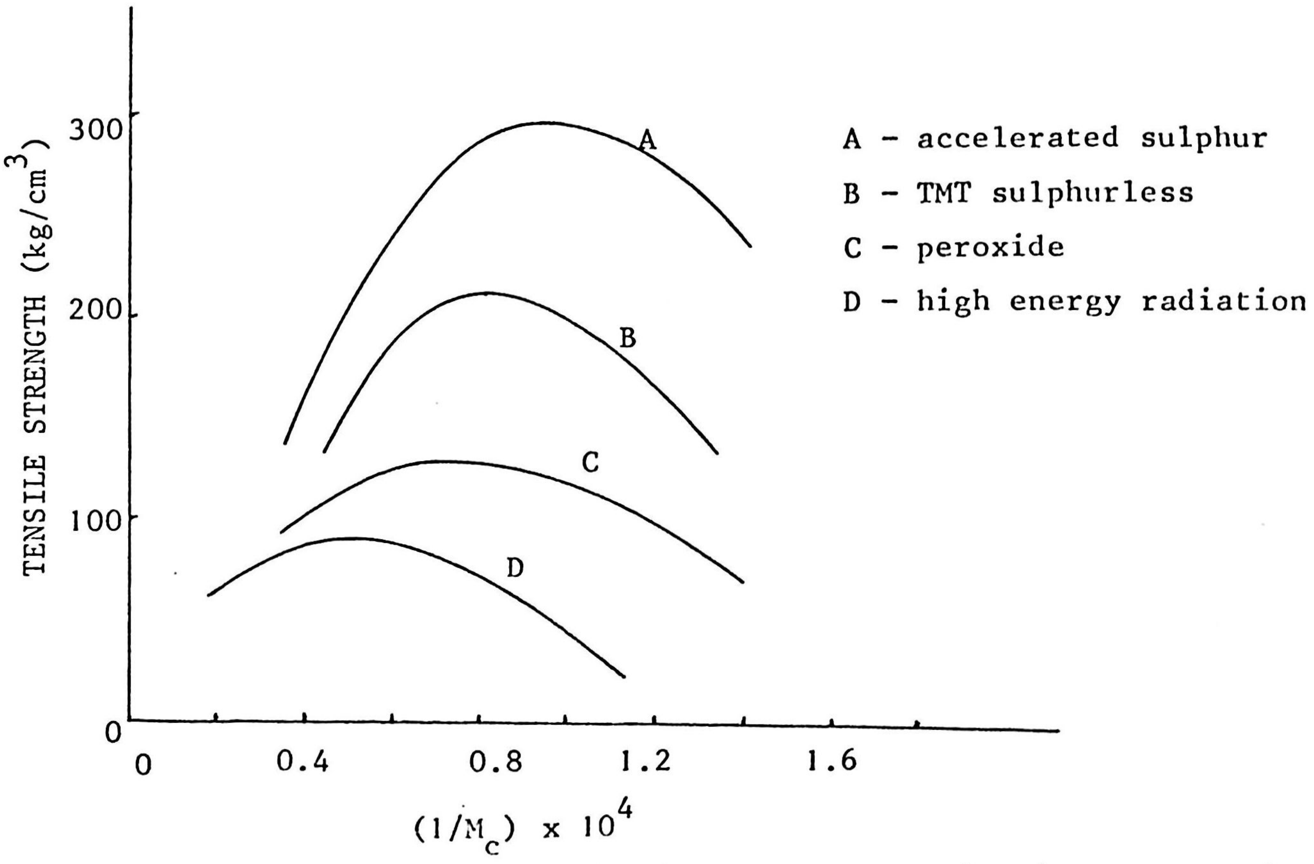


Fig. 1.4: Tensile strength of pure gum NR vulcanizates as a function of $(1/M_c)$ for various vulcanizing systems (Mullins, 1964).

A hypothesis has been developed to account for the relative strengths of vulcanizate with crosslinks of different mechanical strength (Bateman et al., 1963a; Mullins, 1964). Since crosslinks are randomly introduced into the network, they will be unevenly distributed. This will lead to wide variation in the length of chain segments about the mean. Accordingly, when a stress is applied to the network, it will not be evenly supported and will cause some of the chains to be subjected to abnormally high stress because of their unfavourable geometrical disposition. If the crosslinks are mechanically strong, these chains will break leading to an increase in stress on neighbouring chains and, ultimately, catastrophic rupture.

However, if the crosslinks are weaker than the bonds in the main chains (for example S-S bonds), they could relieve localized high stress concentrations permitting a more uniform distribution of stress resulting from the breakages of the weaker bonds. This will prevent the start of the rupture process at relatively low elongation. Hence, it will allow the deformed network as a whole to bear higher stresses at higher elongations.

1.4 Characterisation Of Vulcanizate Structure

1.4.1 Determination of crosslink concentration

The macromolecular structure of a vulcanizate network may be specified in terms of basic network elements, namely network chains (macromolecular segments bound at each end by a crosslink) and chain ends (macromolecular segments bound at one end only to a crosslink). The latter represents network defects arising from the finite molecular weight of the primary rubber molecules. In a network free from chain ends, the relationship between the concentration of network chains and the crosslink density may be determined directly from the functionality of the crosslinks, that is the number of network chains terminated by each crosslink.

For tetrafunctional crosslinks, in the absence of chain ends, each crosslink is associated with one-half of the four network chains bound to it as shown below :

Hence, if M_c is the number average molecular weight of the network chains between crosslinks, $[2M_c/N]$ grams of rubber will contain one crosslink where N is the Avogadro's Number. Therefore, one gram of rubber will contain $[N/(2M_c)]$ crosslinks or $1/(2M_c)$ gram mole of crosslinks.

The parameter, M_c, may be determined experimentally from stress-strain measurements and the use of the relationship E1 (see section 1.3).

$$f/A_o = \rho RTM_c^{-1}(\lambda - \lambda^{-2}) \quad \ldots \text{(E1)}$$

However, in practice, stress-strain relationships are found to deviate considerably from the ideal behaviour predicted by equation E1, and in most cases, it is better described by the Mooney-Rivlin equation (Mooney, 1940; Rivlin & Saunders, 1951) as shown below (E2) :

$$f/2A_o = (C_1 + C_2\lambda^{-1})(\lambda - \lambda^{-2}) \quad \ldots \text{(E2)}$$

where C_1 and C_2 are constants characterising the network. Equation E2 may be rewritten in the form :

$$f/2A_o(\lambda - \lambda^{-2}) = C_1 + C_2\lambda^{-1} \quad \ldots \text{(E3)}$$

At moderate strains, a linear relationship is obtained when results obtained from stress-strain measurements are plotted in the form of $f/2A_o(\lambda - \lambda^{-2})$ versus λ^{-1}. The constants C_1 and C_2 are identified with the intercept and slope respectively.

For vulcanizates swollen in liquid, equation E2 becomes :

$$f/2A_0 = V_1 (C_1 + C_2 \lambda^{-1}) (\lambda - \lambda^{-2}) \ \ldots \ (E4)$$

where V_1 is the volume fraction of rubber vulcanizate in the swollen state. Studies by Gumbrell *et al.* (1953) have shown that C_2 (swollen) progressively decreases to zero as the degree of swelling increases. Thus equation E4 will reduce to equation E1 if

$$C_1 (\text{swollen}) = \rho RT (2M_c)^{-1} \ \ldots \ (E5)$$

In practice, values of C_1 obtained for dry networks are found to agree well with those obtained in the swollen state (Mullins, 1959). Hence, the C_1 values obtained from a dry network may be used to obtain M_c (using equation E5). This will give the number of physically effective crosslinks, provided allowance is made for the effect of chain ends.

Alternatively, M_c can be obtained from equilibrium degree of swelling and the application of the Flory-Rehner equation (Flory & Rehner, 1943), thus :

$$-\ln(1-V_r) - V_r - \chi V_r^2 = \rho V_0 M_c^{-1} (V_r^{1/3}) \ \ldots \ (E6)$$

where V_r is the equilibrium volume fraction of rubber in the swollen network, χ the polymer-solvent interaction parameter, V_o the molar volume of swelling agent, and ρ the density of rubber vulcanizate.

Equation E6 was later modified by Flory(1950) to give :

$$-\ln(1-V_r)-V_r-\chi V_r^2 = \rho V_o M_c^{-1}(V_r^{1/3}-V_r/2) \ldots (E7)$$

By substituting equation E5 into equation E7, an expression could be obtained with C_1, thus :

$$-\ln(1-V_r)-V_r-\chi V_r^2 = 2C_1 V_o (RT)^{-1}(V_r^{1/3}-V_r/2) \ldots (E8)$$

Values of M_c obtained from swelling (equations E6 and E7) and stress-strain measurements (equations E1 and E2) strictly relate to ideal networks of infinite primary molecular weight. Hence allowance has to be made for the presence of chain ends in real networks. In NR, the correction given by Ellis & Welding(1964) takes the form of a replacement of M_c^{-1} in equation E5 by $M_c^{-1}(1-\alpha M_n^{-1}M_c)$ where α is a constant and M_n is the number average molecular weight of the primary molecules.

Although allowance is made for the effect of chain ends, there are doubts concerning the validity of the M_c values as obtained by the above methods. For example, no account is taken of the effect of network entanglements on