

Relationships between Structure and Performance of Vulcanisates

D.S. CAMPBELL* and A.V. CHAPMAN*

Available experimental procedures for estimating chemical crosslink density in rubber vulcanisates and the present state of knowledge of the correlation of chemical crosslink structure with properties of natural rubber vulcanisates are critically assessed. Differentiation is made between correlations with technological test data and with chemical constitution. The difficulties associated with quantitative measurement of chemical crosslink density in gum and filled systems are reviewed and the discussion is amplified by specific reference to published work on the role of polysulphide crosslinks in determining strength properties.

Many correlations exist between sets of technologically relevant properties and between properties and compound formulations, even for a single base polymer. These arise naturally from the necessary accumulation of test data in the course of compound development and process control. To break from this sphere of relationships into one which relates properties to the network chemistry requires different experimental information, which is generally more difficult to acquire. This paper offers a short survey of the experimental and interpretational complexities which must be faced if valid relationships between chemical constitution and vulcanisate performance are to be obtained.

There is a particularly large fund of background knowledge on the vulcanisation chemistry of natural rubber (NR). For this reason, the discussion will concentrate on NR as the base polymer. When the vulcanisates of NR are compared and contrasted with those of other rubbery polymers, two factors must be continually born in mind. The first is the ready ability of NR to crystallise under stress. The effects of crystallisation are widely appreciated and some of its significance will be referred to in later discussion. The second factor is that the chemistry of sulphur vulcanisation of NR differs significantly from that of other diene

rubbers or from that of rubbers from ethylene-propylene copolymers.

The three essential features of the chemistry of a rubber network are the number of chemical crosslinks present, the chemical structure of these crosslinks and the presence or otherwise of non-crosslinking modifications to the polymer backbone. The present discussion will concentrate on assessing the contributions made by the first two of these features to vulcanisate performance, and in the first instance will be concerned with the behaviour of unfilled rubber networks. Some brief mention will also be made of the effects of polymer chain modification and of the presence of fillers.

Crosslink Density

Hardness and stiffness (or modulus) are concepts which are centrally important to performance in even the least sophisticated applications of rubber. Relationships between curative levels and vulcanisate modulus are, therefore, fundamental to all rubber compounding. A high curative level is expected to give a high modulus because it introduces a high level of chemical crosslinks between the polymer chains.

Translation of this sort of qualitative relationship to a quantitative one requires not

* Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford, SG13 8NL, United Kingdom

only a sequence of logical steps, but also a number of quite fundamental assumptions. The translation has been summarised by Saville and Watson¹. For NR, the preferred translation is centred around the Mooney-Rivlin relationship and the Mullins-Moore-Watson calibration of chemical *versus* physical crosslink density. The Mooney-Rivlin relationship empirically describes stress and strain in an elastic network in terms of the two constants C_1 and C_2 (Figure 1). The former is strain-independent and is assumed to be directly related to the concentration of physically effective crosslinks (n_{phys}) as defined by rubber elasticity theory.

Tensile modulus at a single extension is frequently used as a convenient measure of crosslink concentration. In the broadest sense, there is a correlation between the two but the single stress measurement provides no means of assessment of the constant C_2 and hence a proper evaluation of the physically effective crosslinks is not possible. Saville and Watson¹ suggested using two extensional force measurements, MR50 and MR100, to provide some

assessment of the C_2 term and hence give access to the physically effective crosslink density. The approach lacks the precision of the full Mooney-Rivlin treatment but should perhaps receive more attention than it does.

All networks deviate markedly from the Mooney-Rivlin relationship as the network chains approach finite extensibility. This deviation can become apparent at 100% linear extension. Measurements of 200% or 300% modulus contribute to the total extensional force which arises from this effect, and are therefore even less satisfactory for estimating physically effective crosslink densities than the 100% modulus. Swelling in a good solvent for the polymer backbone reduces the constant C_2 and brings the deformation behaviour closer to that predicted by statistical theory. However, finite extensibility of the network chains becomes increasingly important and the force measurements have to be made at very low deformations. Force measurements on swollen samples can take the form of the determination of swollen compression modulus². Experience

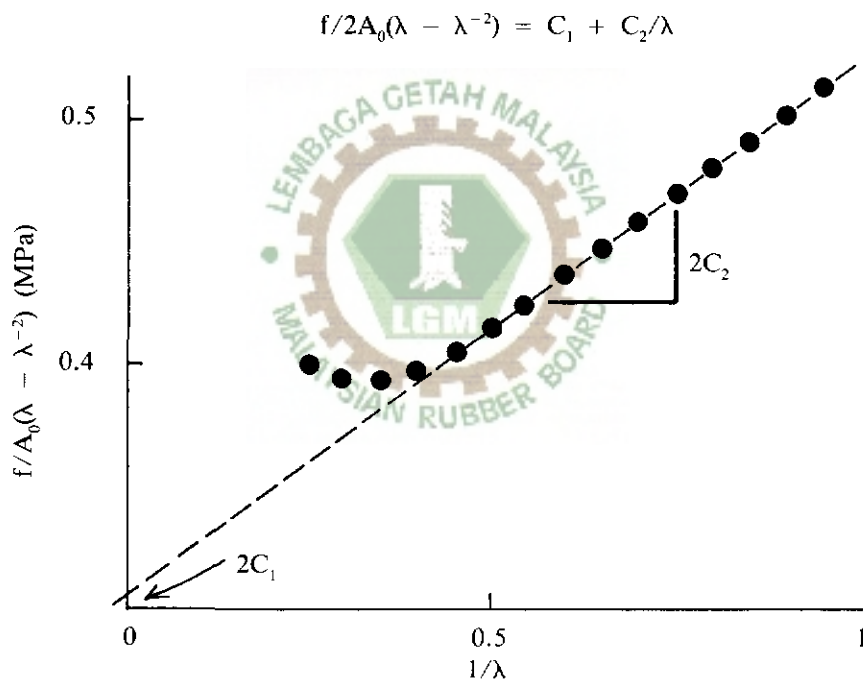


Figure 1. Mooney-Rivlin stress-strain relationship.

suggests, however, that for many samples finite extensibility of the chains intrudes even at the very small deformations used in these experiments.

Physically effective crosslinks are frequently determined from equilibrium swelling measurements using the Flory-Rehner relationship

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = 2\rho V_o n_{phys} v_r^{1/2}$$

where v_r is the volume fraction of rubber in the swollen gel

ρ is the mass per unit volume of network

V_o is the molar volume of the swelling agent

n_{phys} is the concentration of physically effective crosslinks.

The experimentation for this procedure is simple and therefore attractive, but application of the relationship requires assignment of a value for the polymer-solvent interaction parameter, χ . The value used is frequently based on knowledge of the solution behaviour of the uncrosslinked polymer chains, or from combinations of stress-strain and swelling measurements on 'similar' vulcanisates. Table 1 gives some values for the interaction parameter χ for vulcanisates of NR, determined from volume swelling measurements in decane

together with the Mooney-Rivlin measurement of C_1 .

Comparison of the parameters for the two independently prepared but similar sets of vulcanisates with intermediate sulphur to accelerator ratio suggests that values of χ may be reasonably reproducible for any given vulcanisate structure but there is clearly a substantial spread over the whole range of vulcanisate types. Inappropriate use of values of χ from the extremes of the range can result in 15% to 20% errors in calculated physical crosslink densities.

The Mullins-Moore-Watson calibration assumes the validity of determining physically effective crosslink density by either Mooney-Rivlin stress-strain or swelling experiments and evaluates experimentally the separate contributions of chemical crosslinks, chain entanglements and loose chain ends to the elastic behaviour of the network. The correction for chain ends is small in technologically relevant vulcanisates unless there has been excessive breakdown during mixing. However, over this same range of crosslink densities, the correction for physical entanglements is of comparable magnitude to the elastic force arising directly from the presence of the chemical crosslinks.

TABLE 1. POLYMER-SOLVENT INTERACTION PARAMETERS FOR NR NETWORKS

Cure system	S:Acc ratio	Cure time, 140°C (min)	χ (decane)	Reference
None	-	-	0.413 ^a	3
Dicup	-	-	0.411 ± 0.016	4
S/CBS	1:15	-	0.405 ± 0.014	5
S/CBS	1:1.85	-	0.419 ± 0.005	6
S/CBS	1:1.83	-	0.415 ± 0.012	6
S/CBS	1:0.24	30	0.434	6
		40	0.435	
		60	0.439	
		120	0.446	
		240	0.453	

^a From Flory-Fox relationship for limiting viscosity

In recent years, there has been growing interest in the use of modern spectroscopic techniques to provide measures of crosslink density. Progress has come mainly from NMR spectroscopy and has been in two rather different directions. Sophisticated solid state ^{13}C NMR can directly detect signals characteristic of the carbon-sulphur network of vulcanisates⁷ and, in principle, should be able to give direct quantitative measures of network features without recourse to the Mullins-Moore-Watson type of calibration. An alternative and experimentally less demanding, use of NMR is to quantify the line-broadening effect that gelation (crosslinking) has on the main signals from the polymer backbone chain and calibrate this broadening against physically

effective crosslink density⁸. Once a calibration has been obtained, the technique provides an alternative to Mooney-Rivlin stress-strain or volume swelling analysis of networks but retains the need to apply the Mullins-Moore-Watson calibration to evaluate concentration of chemical crosslinks.

The form of the Mullins-Moore-Watson calibration necessarily means that a difference between any two estimates of physically effective crosslinks, caused for example, by a chemical treatment or by a reversion process, disguises a substantially greater percentage change in the concentration of chemical crosslinks, n_{chem} (Figure 2). Relationships which are set up between crosslink type or

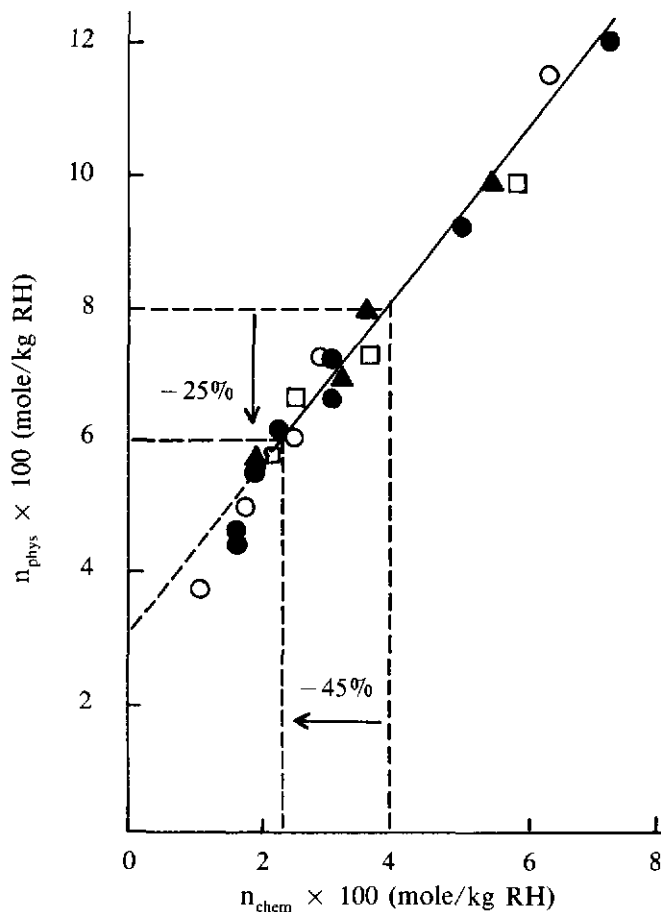


Figure 2. Mullins-Moore-Watson calibration for crosslink density.

crosslink density on the basis of determinations of physically effective crosslinks must inevitably show some distortion relative to the same correlation based on chemical crosslink density.

Table 2 gives qualitative statements about the ways in which common vulcanisate properties depend on the degree of crosslinking^{9,10}. In practice, many of these relationships are secondary ones between the property and the vulcanisate modulus, simply because the amount of technological testing data which is available greatly exceeds the amount of data where the full process of determining chemical crosslink density has been rigorously followed.

Correlation of Strength Properties with Crosslink Type

Some of the properties referred to in *Table 2* are relatively simple in their physical interpretation. Others, such as abrasion resistance, fatigue cracking, tensile strength and tear strength, are considerably more complex, and almost certainly inter-related. Tensile strength is a universally quoted test property for elastomers but is seldom specifically relevant to component service. It is used in a rather indeterminate way to give some indication of the more important properties of tearing resistance and resistance to fatigue cracking. Be this as it may, a large

part of the published work relating failure properties to vulcanisate chemical structure is presented in terms of tensile strength.

Gee¹¹ established the general pattern that tensile strength passes through a maximum with increasing crosslink density. *Figure 3* summarises later information of Bristow and Tiller¹² for vulcanisates of NR obtained using different vulcanisation systems. The results are presented in terms of chemical crosslink density and the curves are characterised by the preponderant crosslink type that is present in the network. The '70% polysulphide' curve describes the behaviour of conventional sulphur-CBS vulcanisates having a sulphur to accelerator ratio of approximately 1:0.25. It is the comparatively high strengths of these materials which supported the belief that weak, interchangeable crosslinks contribute to vulcanisate strength. Bristow and Tiller found that reduction of the sulphur chain length in the crosslinks by treatment with the reagent triphenyl phosphine resulted in a substantial drop in strength and argued that the polysulphide crosslinks were specifically beneficial. On the other hand, Lal¹³ failed to observe strength decreases on similarly treated vulcanisates prepared from a sulphur-diphenylguanidine vulcanisation system and argued, quite legitimately, that crosslink type is not the only network structure

TABLE 2. INFLUENCE OF THE DEGREE OF CHEMICAL CROSSLINKING ON THE PROPERTIES OF A RUBBER NETWORK^a

Property	Change with increase in crosslinking
Stiffness (modulus), hardness	Increase
Breaking elongation	Decrease
Resilience	Increase
Heat build-up	Decrease
Solvent swelling	Decrease
Creep, stress relaxation, set	Decrease
Abrasion resistance	Increase
Fatigue cracking	Increase
Low temperature crystallisation	Decrease in rate
Tensile strength, tear strength	Increase then decrease

^a Reference 10

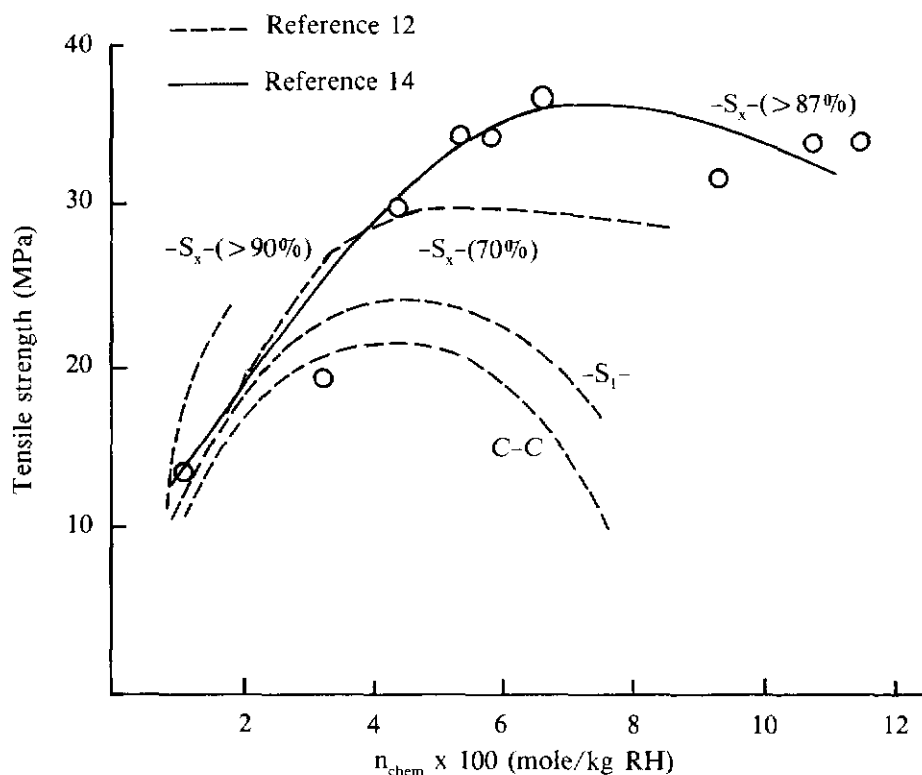


Figure 3. Tensile strength versus crosslink density for $-C-C-$, $-C-S_1-C-$ and $-C-S_x-C-$ networks.

that varies through the series of vulcanisation systems.

Bristow and Tiller obtained a limited number of results for a highly polysulphidic network obtained by vulcanising with an aldehyde/amine condensate and sulphur in the absence of zinc oxide but were unable to maintain this structure to sufficiently high crosslink densities to define a full relationship. The indications were that such a system had potential for very high tensile strength. More recently, Porter¹⁴ succeeded in retaining high polysulphidic character over the full crosslink density range by using the highly active cyclohexylammonium salt of mercaptobenzothiazole (CBM) in place of CBS in a conventional curing recipe and vulcanising for long times at 70°C. These vulcanisates gave high strengths at the higher crosslink densities, but behaved differently

from the unactivated aldehyde/amine cures of Bristow and Tiller at lower crosslink densities (Figure 3).

The absolute values of tensile strength for gum vulcanisates of NR are strongly influenced by the propensity of the NR to crystallise under stress. Breaking forces for gum vulcanisates of NR are five to ten times higher than for gum vulcanisates of non-crystallising rubbers. However, Bristow and Tiller recorded low-temperature crystallisation rates for most of their vulcanisation systems and established that the propensity for low-temperature crystallisation decreases as the strength profiles increase. Although low-temperature crystallisation and stress crystallisation occur on very different time scales and are not necessarily directly correlated, the inverse relation between crystallisation rate and strength, taken in con-

junction with the gross beneficial effect of NR crystallisation under stress, raises the possibility that tensile strength is optimised at some definable crystallisation rate appropriate to the conditions of the tensile strength measurement. Some recent results of Gent¹⁵ on the effect of thiophenol vapour on tearing behaviour give further tentative support for this idea.

Brown *et al.*¹⁶ eliminated the uncertainties of the effects of strain crystallisation by using NR which had been isomerised to its equilibrium *cis-trans* double bond composition to prepare vulcanisates with carbon-carbon, monosulphide or polysulphide crosslinks. These unfilled materials had tensile strengths comparable to those of unfilled SBR or BR vulcanisates (1 – 3 MPa) and were therefore difficult to characterise by simple tensile strength measure-

ment. Their strength properties were assessed by measuring tearing energies over a range of crosslink densities and tearing rates using trouser tear test pieces. The low-temperature CBM vulcanisation system was again used to prepare the highly polysulphidic networks. The results are most readily assessed by comparing tearing energies interpolated to a constant tearing rate (conveniently $10^{-3} \text{ cm s}^{-1}$) and are presented in this form in Figure 4. Shear modulus was used as a measure of crosslink density because determination of the Mooney-Rivlin C_1 constant was complicated by premature failure of samples under tension.

Unlike tensile strength and routinely measured tear strength, tearing energy decreases continuously with increasing modulus¹⁷. The figure shows that there is also a clear depen-

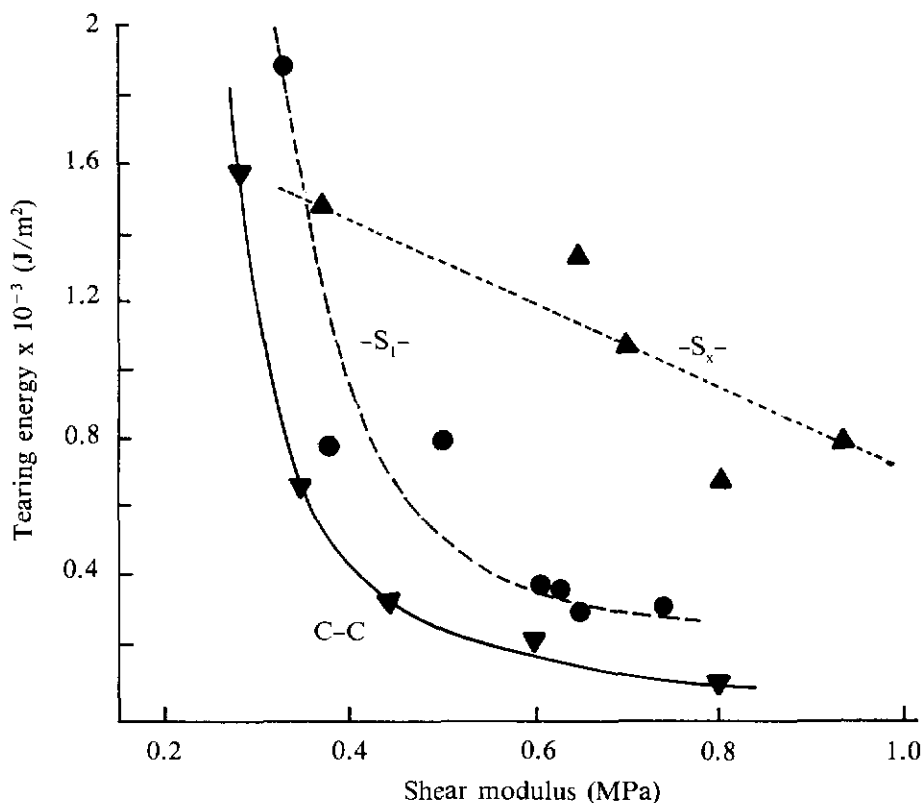


Figure 4. Dependence of tearing energy on crosslink structure for $-C-C-$, $-C-S_1-C-$ and $-C-S_x-C-$ networks (Reference 16).

dence of tearing energy on vulcanisate structure, with the polysulphidic vulcanisates showing consistently higher tearing energies and consequently greater strength. The evidence in support of a positive contribution of polysulphidic crosslinks to strength is therefore enhanced, and is extended beyond the hitherto special case of strain-crystallising networks. Very recently, consistent decreases in tensile strength for both NR and SBR sulphur vulcanisates on treatment with triphenylphosphine have been reported¹⁸, although corresponding changes in tearing behaviour were not claimed. In this work, however, conventional tear strength was measured and the measurement is known to be strongly influenced by variations in modulus.

The positive contribution of polysulphide crosslinks to network strength is usually represented as a consequence of the ease with which the -S-S- bonds can break under stress and rearrange through the network. There has been a suggestion that this bond lability plays its part during the vulcanisation process, allowing localised stresses arising from the moulding operation to be relieved before the end of the vulcanisation. Although moulding stresses are undoubtedly detrimental to strength, it seems that all efforts to minimise such stresses cannot raise a peroxide or EV vulcanisate to the strength levels of a polysulphidic network. A more widely accepted interpretation of the effect of polysulphides is that the -S-S- bond breaking and interchange plays its part during the failure process.

The relatively high level of permanent set exhibited by polysulphidic networks of NR when subjected to high strain is commonly

ascribed to the interchange of polysulphidic bonds and the setting up of a secondary network in the strained state which then suffers compression on release of the strain. Theory exists¹⁹ for the estimation of crosslink breakage and crosslink recombination from the degree of set and the overall change in crosslink density. Brown *et al.*²⁰ have reconfirmed the difference in set behaviour between monosulphidic and polysulphidic networks (*Table 3*) and have shown that the amount of set in a polysulphidic network can be reduced by incorporating a low-molecular-weight tetrasulphide into the network to act as a trap for the sulphur radicals (*Table 4*). Comparisons are made for extracted vulcanisates, vulcanisates swollen with a small amount of inert oil, and vulcanisates swollen with approximately the same amount of a low-molecular-weight tetrasulphide. The tetrasulphide does not materially affect the set behaviour of carbon-carbon crosslinked NR under the same conditions. These experiments were done with normal NR, where stress crystallisation allowed the imposition of large stresses and thus maximised the set behaviour.

Having established that a tetrasulphide can act as a trap for sulphur radicals formed under stress, Brown *et al.* then studied the tearing behaviour of carbon-carbon, monosulphide and polysulphide networks after the same three treatments that were used in the set worked. For this part of the investigation, the effects of crystallisation were removed by using the equilibrium isomerised rubber and tearing energies over a range of tear rates were used as the measure of resistance to failure. The results for vulcanisates with closely comparable shear moduli ($3020 \pm 300 \text{ g/cm}^2$) are summarised in *Figure 5*.

TABLE 3. DEPENDENCE OF PERMANENT SET ON THE PREPONDERANT CROSSLINK TYPE IN NR VULCANISATES

Property	Crosslink type	
	S ₁	S _{>2}
Applied stress (MPa)	13.2	14.7
Resultant strain (% elongation)	735	860
Set (% increase in length)	1.7	9.2

TABLE 4. EFFECT OF A TETRASULPHIDE ON THE PERMANENT SET OF NR VULCANISATES

Vulcanisate treatment	Crosslink type	Extension (%)	Set (%)
Extracted vulcanisates	S_1	735	1.7
Vulcanisates swollen with a small amount of inert oil		720	0.5
Vulcanisates swollen with approximately the same amount of a low-molecular-weight tetrasulphide		727	0.0
Extracted vulcanisates	$S_{>2}$	860	9.2
Vulcanisates swollen with a small amount of inert oil		848	9.0
Vulcanisates swollen with approximately the same amount of a low-molecular-weight tetrasulphide		843	4.4

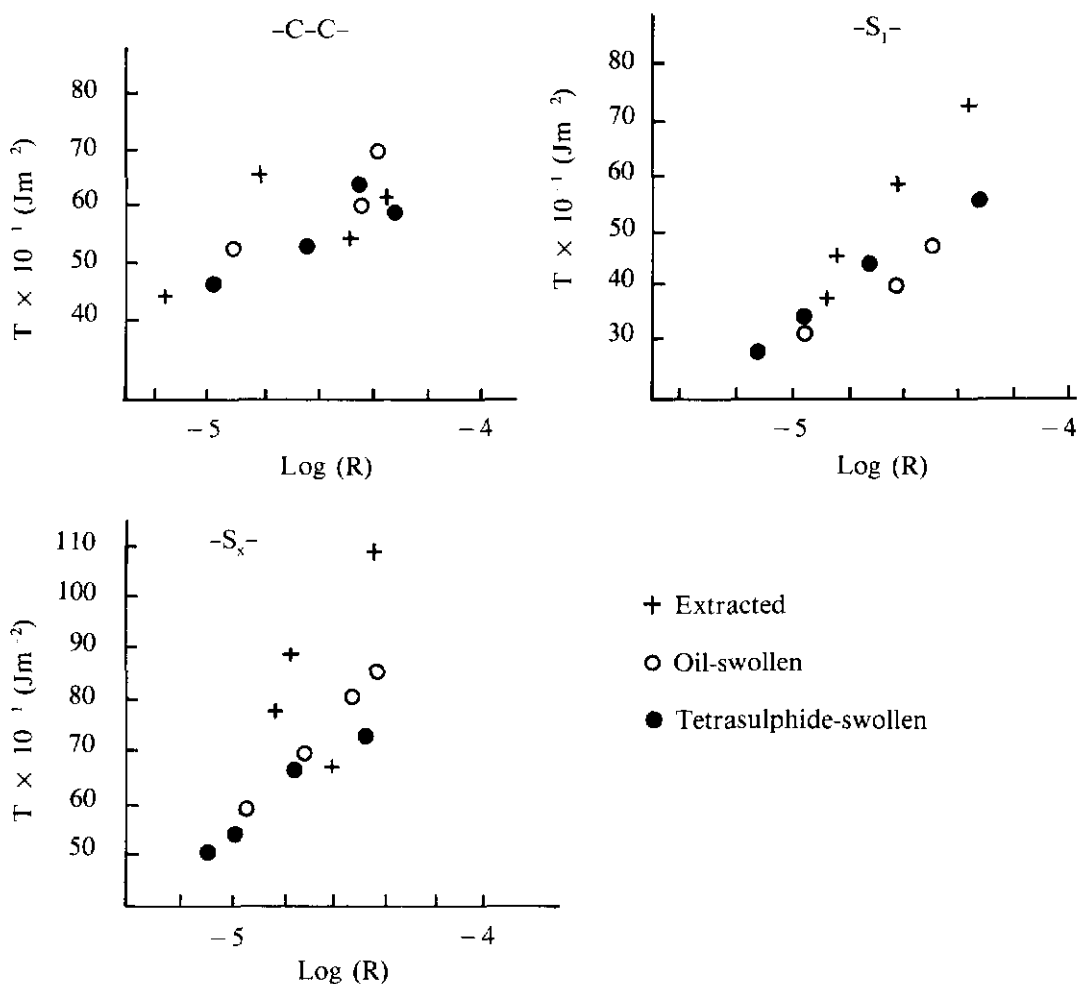


Figure 5. Tearing energy (T) versus $\log(\text{tearing rate}) [\log(R)]$ for $-C-C-$, $-C-S_1-C-$ and $-C-S_x-C-$ networks (Reference 20).

The carbon crosslinked network and the monosulphide network showed small diluent effects on the tearing behaviour for both the oil and the tetrasulphide. The surprising observation was that the polysulphide network also showed no differentiation between the inert diluent and the tetrasulphide. The 'no effect' result of these experiments is of rather less value than the observation of some positive difference, especially in the present case where experimental scatter is high in relation to the differences in tearing energies between the different vulcanisation systems, but the observations, taken with the evidence of the efficacy of the tetrasulphide in trapping broken polysulphide crosslinks and the importance of polysulphide crosslinks in contributing to tearing resistance, indicates that polysulphide breakage is important to strength, but that the recombination is not. In other words, it is not the propensity for crosslink exchange that is important, but simply the presence of crosslinks which are of significantly lower bond energy than the bonds of the polymer backbone.

There is little doubt that polysulphide, and perhaps disulphide, crosslinks confer some specific properties on vulcanisates in addition to their simple existence as ties between the polymer chains, although the interpretation of the mechanisms by which they do so may yet undergo further elaboration. Table 5 summarises the way in which the presence of these crosslink types are thought to influence the performance of vulcanisates¹⁰. Creep, stress

relaxation, set, tensile strength, tear strength and fatigue life are all ultimately associated with the ideas about the presence of labile -S-S- bonds. The beneficial aspects are, however, obtained at some cost to the thermal stability of the network relative to monosulphide or carbon-carbon networks.

Secondary Modifications of the Polymer Chains

Characterisation of networks in terms of crosslink types can be a reasonably successful exercise, albeit time consuming. Characterisation in terms of secondary modification of the polymer chains is much less certain at present. It is necessary to draw evidence from both small-molecule and vulcanisate studies to reach assessments of the type and extent of such modifications in any given vulcanisate. This degree of uncertainty is reflected in an attempt to tabulate chain modification types and levels against properties¹⁰ (Table 6).

The major modifications to the main chains that occur in NR vulcanisation are rearrangement of double bonds, the formation of conjugated olefin and cyclic sulphide structures and the attachment of accelerator residues to the polymer chain. The olefinic and cyclic sulphide modifications arise mainly at longer cure times in the less efficient sulphur vulcanisation systems¹⁰. Attached accelerator residues reach their limiting values near optimum cure and become increasingly relevant as the proportion of accelerator in the mix increases²¹.

TABLE 5. INFLUENCE OF DI- AND POLYSULPHIDE CROSSLINKS ON PROPERTIES OF A RUBBER NETWORK (REFERENCE 10)

Property	Change with increase in di- and polysulphides
Creep, stress relaxation, set	Increase
Incremental swelling	Increase
Tensile strength, tear strength	Increase
Resilience	Increase
Fatigue life	Increase
Heat resistance	Decrease
Thermal ageing resistance	Decrease

TABLE 6. INFLUENCE OF MAIN-CHAIN MODIFICATIONS ON VULCANISATE PROPERTIES (REFERENCE 10)

Property	Change with increase in		
	Unsaturation	Cyclic sulphide	Pendent group
Resilience	Decrease	Decrease	Little effect?
Strength	Decrease	Decrease	Little effect?
Fatigue life	Increase?	Increase?	Little effect?
Swelling in hydrocarbon oils	Decrease?	Decrease	Decrease?
Oxidative ageing resistance	Decrease	Decrease	Decrease?
Low-temperature crystallisation	Rate decrease	Rate decrease	Little effect?

One effect which is of practical significance for NR in some specific applications is the depression of the rate of low-temperature crystallisation. The effect forms the basis of the choice of high-sulphur low-accelerator curing systems for products exposed to sub-zero temperatures.

Filled Networks

In gum vulcanisates, the chemically crosslinked network of polymer chains is overlaid by the chain entanglements which are trapped during the crosslinking reaction. Filled vulcanisates retain the contribution of this 'pure gum' network to their modulus and other properties but there are, in addition, specific effects which arise from the presence of the filler. Inert fillers have, by definition, no effect on the chemistry of network formation but, because of their rigidity, they cause an enhancement of the strain experienced by the elastomeric network, relative to the macroscopic strain applied to the material. This essentially geometric effect is described in the equations of Smallwood²² and Guth²³. The equations can be applied at modest loadings of non-reinforcing fillers to obtain measures of the true strains imposed on the network and thus allow evaluation of Mooney-Rivlin constants. There is therefore a route to characterisation of crosslink densities in such circumstances, but the strain amplification effect results in the incursion of finite extensibility effects at progressively lower macroscopic strains as the filler loading increases.

Reinforcing fillers can be expected to make a similar contribution to the behaviour of the vulcanisate. There are, in addition, contributions which arise from the known chemical interaction between the filler particles and the polymer chains²⁴ and the additional possibility that these fillers can interact with the chemistry of the crosslinking process. The interaction of reinforcing fillers with polymer chains has been the subject of extensive discussion for as long as there has been an interest in characterising the structure of rubber networks. The discussion continues and interpretation of behaviour is still incomplete²⁵. The complex behaviour of reinforcing fillers is directly responsible for inhibiting detailed development of direct experimental correlations between chemical structure and vulcanisate performance in the technologically important black-filled vulcanisates.

The presence of a reinforcing filler essentially negates attempts to determine Mooney-Rivlin constants for the rubber network from stress-strain data. The filler also influences the swelling behaviour and although the interpretation of effects on swelling is subject to uncertainties similar to those associated with stress-strain measurement, Porter^{5,10} has shown that it is possible to obtain an empirical calibration for the restrictive effect of a given carbon black on the degree of swelling. The relationship, expressed in terms of apparent and actual crosslink densities, is of the form:

$$n_{chem} = (n_{chem})_{apparent} / (1 + K_{chem} \Phi)$$

where the apparent value of n_{chem} is the value calculated from the experimentally observed degree of swelling of the filled sample and Φ is the volume fraction of the filler. The constant K_{chem} is characteristic of the filler-polymer combination and is taken to represent the sum of several restrictive effects of the filler on the swelling behaviour of the network. Having established the value of K_{chem} for the filler in question, Porter was able to confirm the conclusions derived from model sulphuration experiments and from other indirect sources that the filler (in this case, N330 black) had an appreciable effect of increasing the efficiency of sulphur crosslinking in a number of vulcanisation systems.

Porter's approach has never been applied to the differentiation of polysulphide, disulphide and monosulphide crosslink types in filled networks. There is uncertainty as to whether it would be legitimate to do so because there is no *a priori* way of deciding whether the constant K_{chem} would be invariant with the chemical treatments required for such differentiation. Our knowledge about the chemical structure of black-filled networks therefore rests largely on that of the corresponding gum vulcanisates, with the extrapolations tempered by the knowledge that black is not entirely innocuous towards sulphur vulcanisation chemistry in that reinforcing blacks are likely to increase vulcanisation efficiency.

CONCLUSIONS

A number of quite fundamental chemical and physical complications prevent ready access to information about the chemical structure of vulcanisate networks from easily available technological information. Correlations between sets of technological results remain the most widely used basis for compound development and process control. The value of the experienced rubber technologist lies in his ability to use these correlations to solve immediate problems. Chemical characterisation of vulcanisates at a molecular level must be seen as complementary to this activity, providing a

means of rationalising the technological information but, because of the added complexities of the experimental techniques, being inappropriate for routine application. The point is illustrated by the amount of effort which has gone into the investigation of the role of polysulphide crosslinks in determining the strength of sulphur vulcanisates.

Increasingly powerful spectroscopic techniques are contributing to our understanding of network chemistry but they have to develop in two distinct ways – qualitative identification of chemical features in a network followed by more quantitative characterisation of their concentrations. Achieving both of these goals will circumvent the difficult process of reliably counting numbers of crosslinks *via* the traditional physical measurements, and give a better characterisation of the secondary modification reactions that are known to have some relevance in vulcanisate performance.

The characterisation of filled networks, especially those containing reinforcing fillers, remains essentially at a micro-physical level rather than a chemical level because of the complexities of adequately describing the physical effects of the filler. The limited chemical evidence that exists suggests that the vulcanisation chemistry of gum systems can be used as a reasonable base for the description of the filled vulcanisates, and it is generally assumed that correlations that have been established between performance and network structure for gum vulcanisates bear some relationship to the performance of filled vulcanisates.

Date of receipt: March 1990
Date of acceptance: June 1990

REFERENCES

1. SAVILLE, B. AND WATSON A.A. (1967) Structural Characterization of Sulphur Vulcanized Rubber Networks. *Rubb. Chem. Technol.*, **40**, 100.
2. SMITH, D.A. (1967) Micromethod for Estimation of the Degree of Crosslinking in Elastomers from Compression Modulus of Swollen Vulcanisates. *J. Polym. Sci.*, **C16**, 525.

3. BRISTOW, G.M. AND WATSON, W.F. (1958) Viscosity - Equilibrium Swelling Correlations for Natural Rubber. *Trans. Farad. Soc.*, **54**, 1567.
4. BRISTOW, G.M. (1965) Relation between Stress-Strain Behaviour and Equilibrium Volume Swelling for Peroxide Vulcanisates of Natural Rubber and *cis*-1,4-Polyisoprene. *J. appl. Polym. Sci.*, **9**, 1571.
5. PORTER, M. (1967) Structural Characterization of Filled Vulcanisates. Part I. Determination of the Concentration of Chemical Crosslinks in Natural Rubber Vulcanisates Containing High Abrasion Furnace Black. *Rubb. Chem. Technol.*, **40**, 866.
6. CAMPBELL, D.S. Unpublished Data. Malaysian Rubber Producers' Research Association, U.K.
7. ANDREIS, M. AND KOENIG, J.L. (1989) Application of NMR to Crosslinked Polymer Systems. *Advances in Polymer Science*, **89**, 69.
8. TINKER, A.J. AND LOADMAN, M.J.R. (1989) The Application of Swollen-State CW-¹H NMR Spectroscopy to the Estimation of the Extent of Crosslinking in Vulcanized Polymer Blends. *Rubb. Chem. Technol.*, **62**, 234.
9. MORRISON, N.J. AND PORTER, M. (1984) Temperature Effects on the Stability of Intermediates and Crosslinks in Sulphur Vulcanization. *Rubb. Chem. Technol.*, **57**, 63.
10. CHAPMAN, A.V. AND PORTER, M. (1988) Sulphur Vulcanization Chemistry. *Natural Rubber Science and Technology* (Roberts, A.D. ed), p. 511. Oxford: Oxford University Press.
11. GEE, G. (1947) Tensile Strengths of Pure Gum Natural Rubber Compounds. *J. Polym. Sci.*, **2**, 451.
12. BRISTOW, G.M. AND TILLER, R.F. (1970) Correlation of Structure and Properties of Natural Rubber Vulcanisates. *Kautschuk Gummi*, **25**, 55.
13. LAL, J. (1970) Effect of Crosslink Structure on Properties of Natural Rubber. *Rubb. Chem. Technol.*, **43**, 664.
14. BROWN, P.S., PORTER, M. AND THOMAS, A.G. (1985) Influence of Crosslink Structure on Properties in Crystallising and Non-crystallising Polyisoprenes. *Proc. Int. Rubb. Conf. Kuala Lumpur*, 1985, **2**, 20.
15. GENT, A.N. AND HINDI, M. (1989) Effect of Oxygen on the Tear Strength of Elastomers. *ACS Rubber Division, Spring Meeting, Mexico City*, 1989, Paper 48.
16. BROWN, P.S., PORTER, M. AND THOMAS, A.G. (1987) The Dependence of Strength Properties on Crosslink Structure in Vulcanized Polyisoprenes. *Kautschuk Gummi*, **40**, 17.
17. LAKE, G.J. AND THOMAS, A.G. (1988) Strength Properties of Rubber. *Natural Rubber Science and Technology* (Roberts, A.D. ed), p. 731. Oxford: Oxford University Press.
18. NASIR, M. AND TEH, G.K. (1988) The Effects of Various Types of Crosslinks on the Physical Properties of Natural Rubber. *Eur. Polym. J.*, **24**, 733.
19. THOMAS, A.G. (1974) Factors Influencing the Strength of Rubbers. *J. Polym. Sci.*, **C48**, 145.
20. BROWN, P.S., PORTER, M. AND THOMAS, A.G. (1987) The Role of Crosslink Breakage in Determining the Strength of Vulcanisates. *Proc. Int. Rubb. Conf. Harrogate 1987*, Paper 18A.
21. CAMPBELL, D.S. (1970) Structural Characterization of Vulcanisates. XI. Network-Bound Accelerator Residues. *J. appl. Polym. Sci.*, **14**, 1409.
22. SMALLWOOD, H.M. (1944) Limiting Law of the Reinforcement of Rubber. *J. appl. Phys.*, **15**, 758.
23. GUTH, E. (1945) Theory of Filler Reinforcement. *Rubb. Chem. Technol.*, **18**, 596.
24. KRAUS, G. (1978) Reinforcement of Elastomers by Carbon Black. *Rubb. Chem. Technol.*, **51**, 297.
25. HAMED, G.R. AND HATFIELD, S. (1989) On the Role of Bound Rubber in Carbon Black Reinforcement. *Rubb. Chem. Technol.*, **62**, 143.