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Structural Characterisation of Naturally Occurring Trans-Polyisoprenes

YASUYUKI TANAKA*, MAKIO MORI*, ATSUSHI TAKEI*,
PLOENPIT BOOCHATHUM* AND YOSHINORI SATO**

The structure of trans-polyisoprene isolated from Chicle latex and Gutta percha latex was analysed by ^{13}C -NMR spectroscopy. The trans-polyisoprene from Chicle latex showed the ^{13}C -NMR signals characteristic of the dimethylallyl terminal unit (ω -terminal) and trans-isoprene unit terminated with hydroxyl and ester groups (α -terminal). The ester terminal group was not detected in the trans-polyisoprene from Chicle resin. The degree of polymerisation estimated from the intensity ratio of the signals from internal trans units and ω -terminal group was in fair agreement with the value obtained by GPC-LALLS measurement. However, the intensity ratio of signals from the ω -terminal and α -terminal groups was found to be 1/0.76, indicating the loss of a part of α -terminal in the latex sample. The trans-polyisoprene from Gutta percha latex showed a similar ^{13}C -NMR spectrum as that from Chicle. The loss of the α -terminal was also observed for the trans-polyisoprene from Gutta percha latex. It was presumed that a chemical or biochemical modification of α -terminal groups occurred during storage of the latex.

Few species of higher plants have been shown to produce polyisoprene of *trans*-1, 4 configuration. Gutta percha from *Palaquium gutta* and Balata from *Mamusops balata* are typical *trans*-polyisoprene occurring as latex. *Achras sapota* is known to contain two types of polyisoprenes in *trans* and *cis* configurations, called Chicle. It was proved by ^{13}C -NMR analysis that Chicle polyisoprene is a mixture of *trans*-polyisoprene and *cis*-polyisoprene^{1,2}.

The authors have investigated the terminal groups and alignment of isoprene units in naturally occurring *cis*-polyisoprenes by using the ^{13}C -NMR method which was established on the basis of ^{13}C -NMR analysis of acyclic terpenes and polyprenols³. It has been found that *cis*-polyisoprenes isolated from the leaves of Goldenrod and Sunflower are a high molecular weight homologue of polyprenol consisting of a dimethylallyl terminal unit, of about three *trans* units, and a long sequence of *cis* units terminated with hydroxyl or ester

group aligned in that order^{4,5,6}. However, *cis*-polyisoprenes occurring as latex such as *Hevea* rubber, Jelutong rubber, and Sorvinha rubber were found to have both terminal groups different from polyprenols and terpenes⁷. On the other hand, *cis*-polyisoprene from mushroom was found to be a high molecular weight homologue of two-*trans* polyprenol containing a dimethylallyl unit and an ester terminal group, despite the fact that it exudes from sporophores as latex⁸. In addition, a significant decrease of both terminal units was observed when sporophores were stored a few days after harvesting. This implies that the absence of both terminal groups in rubbers occurring as latex correlates with the period of storage in laticiferous cells and that after collection.

This paper reports on the structural characterisation of *trans*-polyisoprenes obtained from the latices of Chicle and Gutta percha by using the ^{13}C -NMR method. The quantities

* Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

** Lotte Central Laboratory Co. Ltd., Numakage, Urawa, Saitama 336, Japan

of both terminal units were checked by comparing the degree of polymerisation from the ^{13}C -NMR measurement with that from the GPC-LALLS.

EXPERIMENTAL

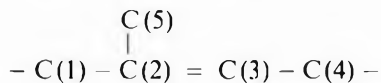
Fresh Chicle latex collected from a single tree in Quintana-Roo, Mexico was subjected to purification two weeks after collection by tapping. The resinous fraction was removed by Soxhlet extraction with acetone from the partially coagulated latex sample. Commercially obtained Chicle resin was utilised as a reference sample. Pure *trans*-polyisoprene was separated from *cis*-polyisoprene by repeated recrystallisation from hexane solution at 40°C. Gutta percha latex was collected from a single tree in Sumatra, Indonesia. Three weeks after collection, spontaneously coagulated Gutta percha latex, was purified by reprecipitation from toluene solution with methanol, followed by Soxhlet extraction with acetone under nitrogen atmosphere. *Trans*-polyisoprene from Gutta percha latex was further purified by repeated recrystallisation in hexane. Low molecular weight fractions of Gutta percha latex were obtained by fractional precipitation in toluene/methanol. GPC-LALLS measurements were done with a JASCO 880-PU high pressure pump and a TOSOH LS-8000 low-angle laser light scattering photometer (LALLS) equipped with a TOSOH RI-8011 detector. Molecular weights of *trans*-polyisoprene samples were determined by using standard polystyrene samples. The ^{13}C -NMR measurements were done on a JEOL FX-200 at 50.1 MHz in CDCl_3 at 50°C using a pulse repetition time of 6 s for 50° pulse.

RESULTS

Trans-polyisoprene from Chicle Latex

The molecular weight of *trans*-polyisoprene from Chicle latex was found to be $\bar{M}_w = 14 \times 10^3$ and $\bar{M}_n = 7.8 \times 10^3$ by GPC-LALLS measurement. In the ^{13}C -NMR spectrum of Chicle *trans*-polyisoprene, small signals characteristic of the dimethylallyl terminal unit (ω -terminal) at 17.64 p.p.m. (C-5 CH_3) and 25.61 p.p.m. (C-1 CH_3) and the terminal *trans* unit linked to hydroxyl group

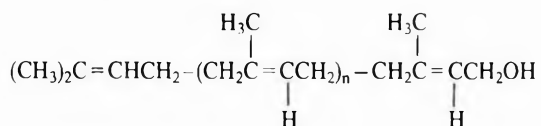
(α -terminal) at 59.44 p.p.m. (C-4 CH_2OH) were observed as shown in *Figure 1*. Here, the carbon atoms in isoprene units including both the terminal units are designated as follows:



In this spectrum, very small signals were detected at 61.32 and 29.70 p.p.m. The latter signal is assigned to the methylene carbon atoms in the $(\text{CH}_2)_n$ sequence. The former is assignable to a ω C-4 carbon linked to a fatty acid ester group. But other signals characteristic of saturated fatty acid ester groups, *i.e.* OCOCH_2 around 34 p.p.m. and methyl carbon signals around 14 p.p.m., were not detected due to trace amounts of the ester group. The intensity ratio of the signals at 61.32 and 59.44 p.p.m. indicates that about 15% of the α -terminal unit is esterified in the sample. These signals were also detected in the ^{13}C -NMR spectrum of *trans*-polyisoprene obtained from Chicle latex from different sources⁹. On the other hand, these signals were not observed in the spectrum of the sample from Chicle resin as shown in *Figure 1*. These findings indicate that the latex samples suffered a small amount of esterification during storage after collection or during storage in laticiferous cells.

The relative intensity of the *trans* C-1 methylene carbon signal and ω C-1 methylene carbon signal was found to be 140, which is in fair agreement with the degree of polymerisation of 120 determined by the GPC-LALLS measurement. The intensity ratio between the ω C-1 signal at 25.61 p.p.m. and the α C-4 signals at 61.32 and 59.44 p.p.m. was found to be 1/0.76. In the case of *trans*-polyisoprene from Chicle resin, which was usually coagulated directly after collection, the intensity ratios of the corresponding ω and α signals were found to be 1/1.05 for unfractionated samples and 1/0.91 for fractionated samples². This indicates that *trans*-polyisoprene from Chicle latex has fundamentally the same structure as that from Chicle resin as shown below, although it is anticipated that a part of the hydroxyl terminal

group would be modified during storage resulting in the loss of hydroxyl and/or ester groups:



Trans-polyisoprene from Gutta Percha Latex

The molecular weight of *trans*-polyisoprene from Gutta percha latex was found to be $\bar{M}_w = 12 \times 10^4$ and $\bar{M}_n = 48 \times 10^3$ by GPC-LALLS measurement. The ultimate fraction of fractional precipitation was subjected to ^{13}C -NMR analysis. The low molecular weight fraction showed fundamentally the same ^{13}C -NMR signals as Chile *trans*-polyisoprene. As shown in Figure 2, the ω -terminal unit showed characteristic signals at 17.61 p.p.m. (C-5), 25.61 p.p.m. (C-1), and

131.05 p.p.m. (C-2). Similarly, the signals at 59.36 and 139.52 p.p.m. were assigned to the C-4 and C-2 carbon atoms in the α -terminal unit, respectively. Signals from an ester group were not detected in the spectrum.

The degree of polymerisation estimated from the intensity ratio between the *trans* C-1 CH_2 and α C-4 CH_2 signals was found to be 760, which is higher than that of 510 determined by GPC-LALLS. Although the accurate relative intensity of the α C-1 signal was not obtained due to a poor resolution of the spectrum, the height of the signal is apparently lower than that of the α C-4 signal. The loss of the α -terminal signal was also observed for a commercially obtained Gutta percha solid sample⁹. This may imply the presence of a similar modification of both terminal units as in the case of *cis*-polyisoprene occurring as latex⁷. Commercially obtained Gutta percha resin showed small signals arising from epoxide groups and *cis*-polyisoprene⁹, while

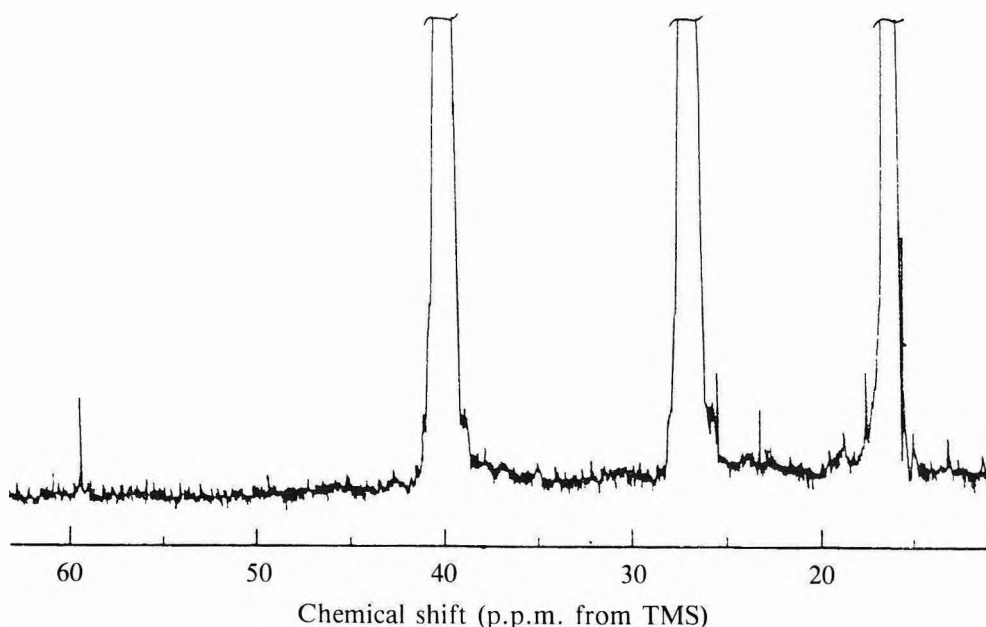


Figure 2. ^{13}C -NMR spectrum of low molecular weight *trans*-polyisoprene from Gutta percha latex.

no signal due to these impurities was detected in the latex sample. These findings demonstrate that the fundamental structure of *trans*-polyisoprene from Gutta percha is the same as that of Chicle *trans*-polyisoprene and the biosynthesis proceeds in a similar way.

DISCUSSION

The biosynthesis of *trans*-polyisoprene in Chicle is assumed to start from dimethylallyl pyrophosphate and proceeds by the successive addition of isopentenyl pyrophosphate to polyisoprenyl pyrophosphate². The termination step is presumed to occur by dephosphorylation to form the hydroxyl α -terminal group. The presence of hydroxyl and ester α -terminal groups was clearly observed in *cis*-polyisoprene from the leaves of Sunflower formed in non-laticiferous cells^{4,6}. Hydroxyl and ester terminal groups are in common to polyprenols, which consist of nine to twenty-three isoprene units widely distributed in higher plants¹⁰. On the other hand, these types of α -terminal groups and dimethylallyl terminal unit were not detected in *cis*-polyisoprene occurring as latex such as *Hevea* rubber^{5,7,9}. The decrease of the dimethylallyl terminal unit as well as the α -terminal groups was also observed in *cis*-polyisoprene occurring as latex from mushroom during storage of sporophores⁸. These findings suggest that the α -terminal unit with hydroxyl or ester group is labile and readily chemically or biochemically modified in latex during storage resulting in loss of the functional groups.

A set of dimethylallyl and α -terminal units was detected in the case of *trans*-polyisoprene from Chicle. However, a part of the hydroxyl terminal group was replaced by the fatty acid ester group in Chicle latex stored two weeks after collection. Apparent reduction of α -terminal group was observed in the case of Gutta percha latex. These findings indicate that some chemical or biochemical reaction proceeds in latex to modify the terminal unit

as in the case of *cis*-polyisoprene occurring as latex.

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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

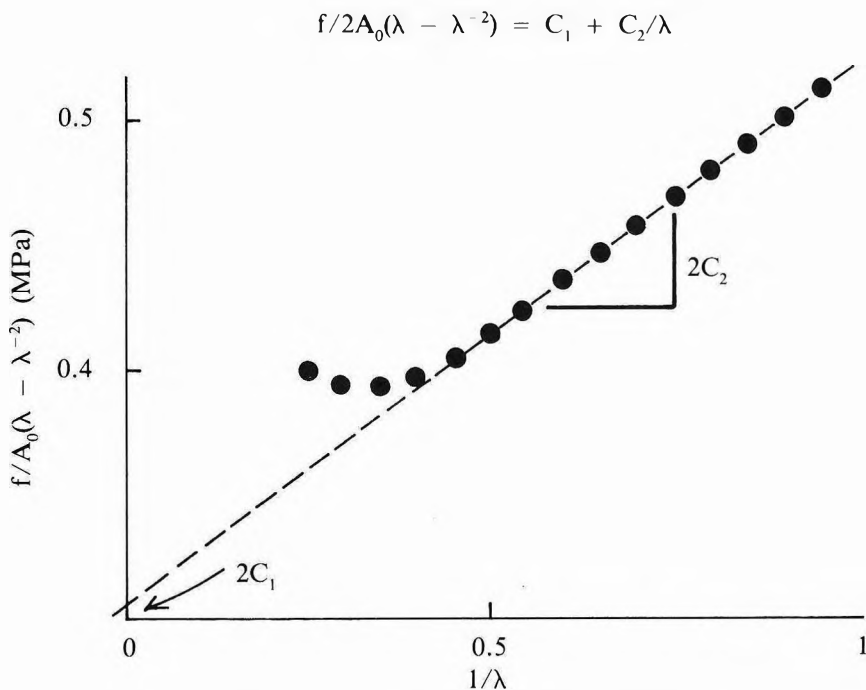


Figure 1. Mooney-Rivlin stress-strain relationship.

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

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = 2\rho V_o n_{phys} v_r^{1/3}$$

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

ρ is the mass per unit volume of the 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

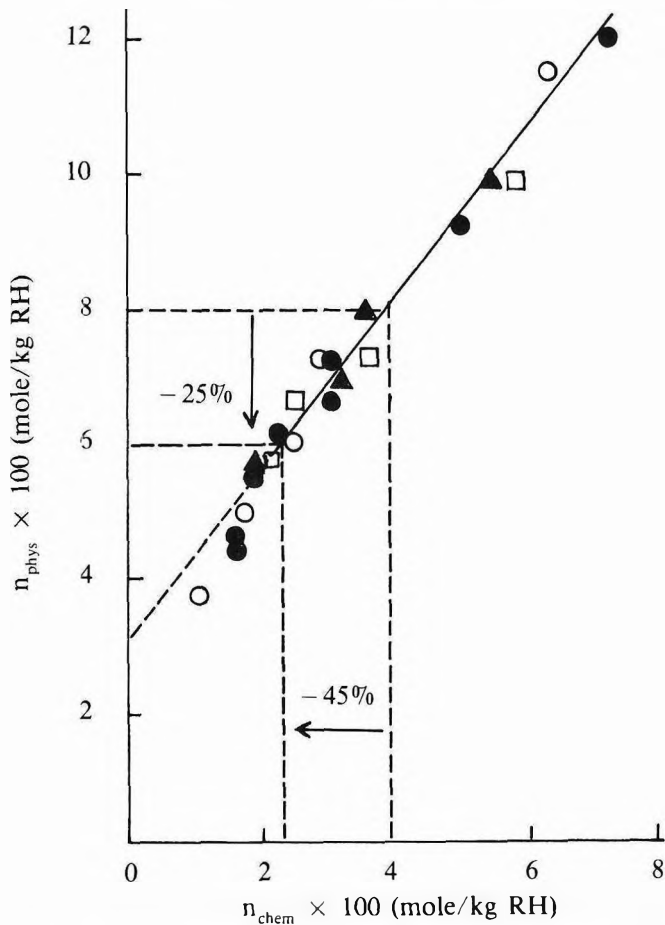


Figure 2. Mullins-Moore-Watson calibration for crosslink density.

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 describe 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

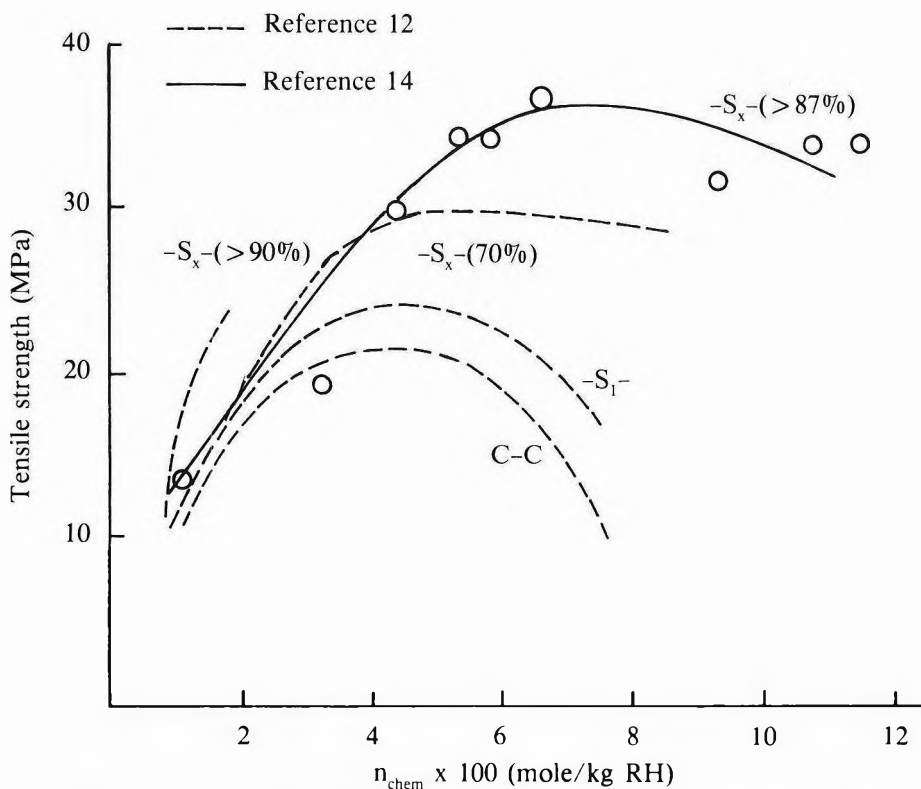


Figure 3. Tensile strength versus crosslink density for $-C-C-$, $-C-S_1-C-$ and $-C-S_x-C-$ networks.

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-

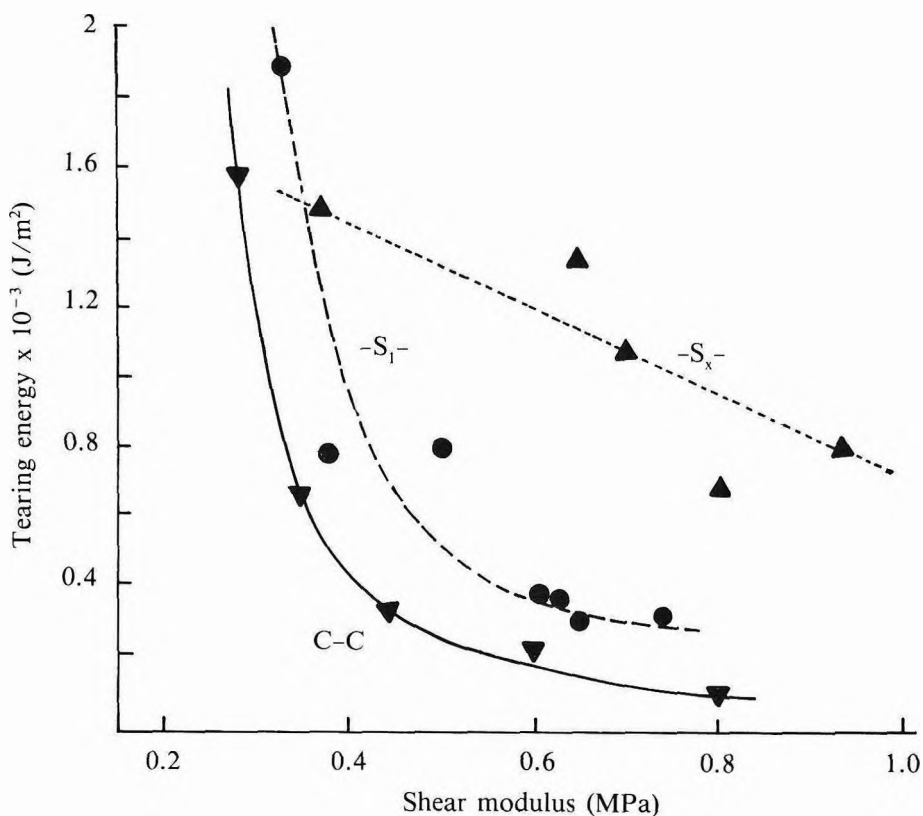


Figure 4. Dependence of tearing energy on crosslink structure for $-C-C-$, $-C-S_1-C-$ and $-C-S_x-C-$ networks (Reference 16).

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

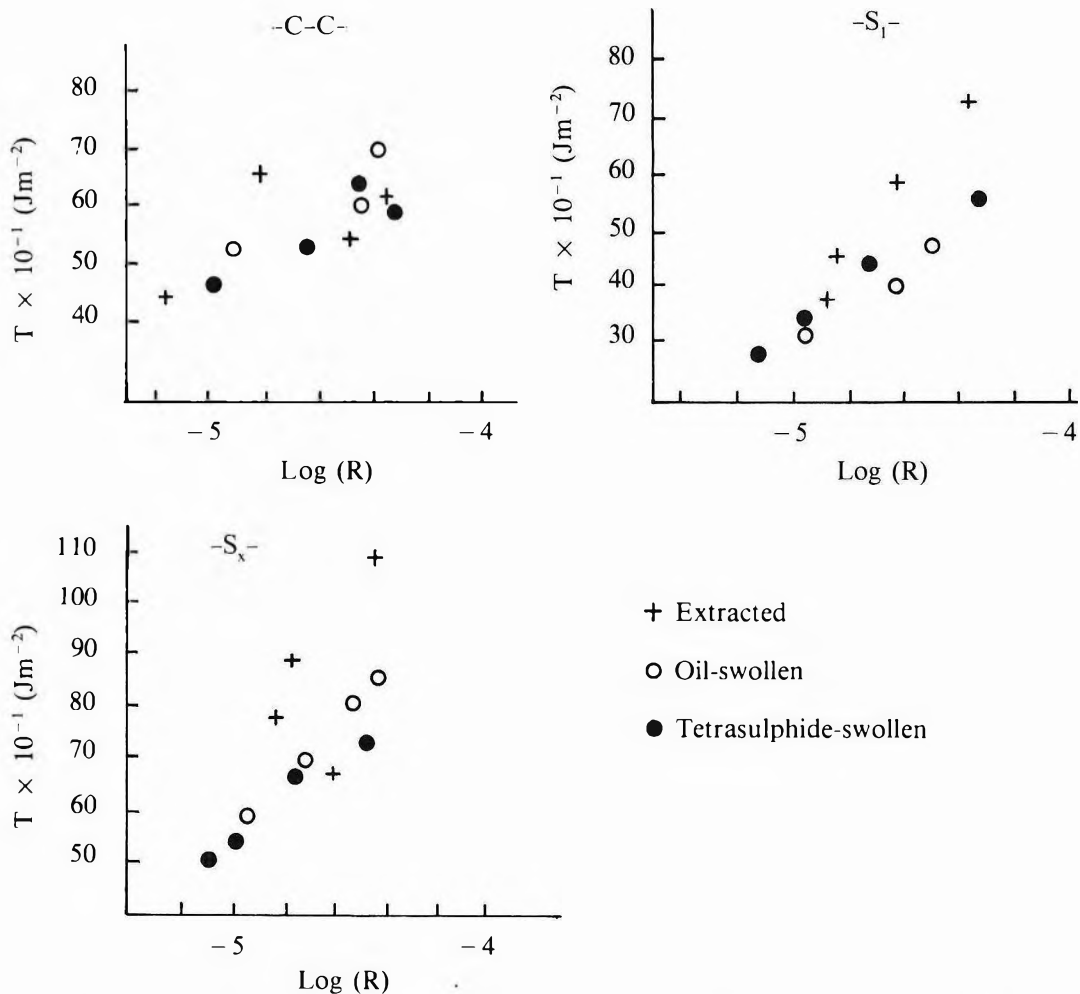


Figure 5. Tearing energy (T) versus $\log(\text{tearing rate}) [\log(R)]$ for $-C-C-$, $-C-S_1-C-$ and $-C-S_x-C-$ networks (Reference 20).

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.

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A Facile Reaction of Sulphenamide Accelerators with Acetone

A.V. CHAPMAN*

N-cyclohexylaminobenzothiazole-2-sulphenamide (CBS) reacts with acetone at ambient temperature to give 2' (benzothiazolythio) propan-2-one (1), 1, 1-bis-(2'-benzothiazolythio)-2-cyclohexylaminoprop-1-ene (2), cyclohexylamine, and a trace of 2-mercaptobenzothiazole (MBT). 1 is an intermediate in the production of 2, as it reacts with CBS in the absence of acetone to give 2. 1, 3-bis-(2'-benzothiazolythio) propan-2-one (3) and 1, 1-bis-(2'-benzothiazolythio) propan-2-one (4) are also produced in the latter reaction. This reactivity of sulphenamide accelerators should be borne in mind when employing acetone extraction in the analysis of curatives in rubber compounds or vulcanisates.

Determination of added curatives in compounded but unvulcanised natural rubber normally involves extraction with acetone at ambient temperature¹. Extraction at higher temperatures is usually avoided because of potential chemical changes in the curatives. In particular, thiuram disulphides are known to undergo decomposition in acetone to give dithiocarbamates². Recently, Jefferson *et al.*³ observed that tetramethylthiuram disulphide (TMTD) itself reacts slowly with acetone at ambient temperature to give the thiocarbamoylthioprop-2-one (7). Presumably, this mode of reaction is also the source of the dithiocarbamates.

During the course of an investigation on the reactions of cyclohexylamine with di-2-benzothiazolyl disulphide (MBTS), two minor products were isolated from a reaction at 50°C in cyclohexane. One of these was identified as 2'-benzothiazolythioprop-2-one (1). The second was eventually shown to be the enamine (2). The other products obtained were *N*-cyclohexylbenzothiazole-2-sulphenamide (CBS), 2-mercaptobenzothiazole (MBT) and the cyclohexylammonium salt (CBM) of MBT. There was also some unreacted MBTS. It was believed that the two unexpected products arose from reaction of either MBTS or CBS with acetone which had been used for the separation of the products. To investigate

this further, the reactivity of acetone towards MBTS and CBS was studied.

MATERIALS AND METHODS

NMR spectra were recorded on a Perkin-Elmer R32 90MHz, a Varian XL200, a Varian VXR-400, or a General Electric QE 300 instrument using tetramethylsilane as the internal standard. I.r. spectra were recorded on a Perkin-Elmer 157 or 377 spectrophotometer. Melting points were obtained on a Mettler hot-stage microscope. The progress of reactions was followed and purity of compounds checked by analytical t.l.c. using Merck silica gel 60 F₂₅₄ pre-coated plates. Merck silica gel 60 (40 - 63 μm) was used for preparative column chromatography. C, H and N micro-analysis was performed on a Perkin-Elmer 240 instrument. U.v. spectra were recorded on a Pye Unicam SP8-100 spectrophotometer. The solvent was evaporated using a rotary evaporator at reduced pressure (typically 40 mm Hg).

MBTS was recrystallised twice from toluene, melting point (m.p.) 179°C - 179.8°C. CBS was recrystallised from cyclohexane. Acetone, cyclohexane, toluene, ethanol, diethyl ether and petroleum ether were of A.R. grade. The cyclohexylamine was redistilled from CaH₂, boiling point (b.p.) 66°C - 68°C at 84 mm Hg.

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

Reaction of MBTS with Cyclohexylamine

MBTS (665 mg, 2.00 mmol), cyclohexylamine (397 mg, 4.01 mmol) and cyclohexane (4.00 g) were combined in a Carius tube, de-gassed and sealed under vacuum. The tube was shaken at $50^{\circ}\text{C} \pm 0.3^{\circ}\text{C}$ for 160.5 h. The solid was filtered off and washed with cyclohexane. The solvent was evaporated from the filtrate and the residue eluted with dichloromethane on a silica gel column. The principal fraction obtained was CBS (129 mg, 24%), mixed with a small amount of MBTS, and was recrystallised from petroleum ether (b.p. $60^{\circ}\text{C} - 80^{\circ}\text{C}$), m.p. $100.4^{\circ}\text{C} - 100.8^{\circ}\text{C}$ (Reference 4, $103^{\circ}\text{C} - 104^{\circ}\text{C}$); the i.r. spectrum was identical with the reference spectrum.

Dichloromethane (20 cm^3) was added to the solid from the reaction mixture and the mixture heated to boiling. On cooling, the solid (281 mg) was filtered off. By h.p.l.c. analysis [eluting with MeCN/ H_2O (70:30) through octadecylsilica gel], this was by weight 59% MBTS, a maximum of 27% of the cyclohexylammonium salt (CBM) of MBT and a minimum of 14% MBT (CBM gives MBT on h.p.l.c. analysis). Acetone (5 cm^3) was added to the filtrate: there was no further precipitation. The solvent was evaporated and boiling dichloromethane (5 cm^3) added to the residue. On cooling, a solid was filtered off. By h.p.l.c. analysis, this was by weight 3.2% MBTS (26 mol% in total recovered), a maximum of 73% CBM (a maximum of 32 mol% altogether), and a minimum of 24% MBT (a minimum of 21 mol% altogether). The filtrate was eluted with dichloromethane on a silica gel column. Three main fractions (19, 91 and 70 mg) were collected. The second was purified by elution with dichloromethane through a second silica gel column and then recrystallised from petroleum ether (b.p. $40^{\circ}\text{C} - 60^{\circ}\text{C}$) giving 2'-benzothiazolythiopropion-2-one (**1**) (23.3 mg, 5.2%), m.p. $68^{\circ}\text{C} - 69^{\circ}\text{C}$ (Reference 5, $70^{\circ}\text{C} - 71^{\circ}\text{C}$); ν_{max} (KBr) 2960, 1725 (CO), 1470, 1435, 1365, 1320, 1300, 1280, 1240, 1005 (C-S), and 760 cm^{-1} (Reference 5, 1720 cm^{-1}); δ_{H} (90 MHz; CDCl_3) 2.35 (3H, s, CH_3), 4.20 (2H, s, CH_2), and 7.2-7.9 (4H, m, ArH). The third fraction was recrystallised from ethyl

acetate giving 1, 1-bis-(2'-benzothiazolythio)-2-cyclo-hexylaminoprop-1-ene (**2**) (16.9 mg, 3.6%), m.p. $206^{\circ}\text{C} - 207^{\circ}\text{C}$ (with some decomposition). It can be further recrystallised from acetone raising the m.p. to $209.8^{\circ}\text{C} - 210.2^{\circ}\text{C}$ (Found: C, 59.0; H, 5.0; N, 9.2. $\text{C}_{23}\text{H}_{23}\text{N}_3\text{S}_4$ requires C, 58.8; H, 4.9; N, 8.9%); ν_{max} (KBr) 3240 (NH), 2930, 2850, 1560, 1460, 1425, 1005 (C-S), 760, 750 and 725 cm^{-1} ; λ_{max} (EtOH) 226 nm; δ_{H} (200 MHz; CDCl_3) 1.0-2.0 [10H, m, (CH_2)₅], 2.46 (3H, s, CH_3), 3.39 (1H, m, NCH), 6.34 (1H, d, J 9 Hz, NH, exchanges with D_2O), 7.29 and 7.41 (4H, 2xt, J 7 Hz, 5'-H and 6'-H), 7.76 (2H, d, J 8 Hz, 4'-H or 7'-H) and 7.85 (2H, dd, J 8 and 3 Hz, 4'-H or 7'-H); δ_{C} (50.3 MHz; CDCl_3) 24.7 (cyclohexyl C-3 and C-5), 25.1 (cyclohexyl C-4), 34.3 (cyclohexyl C-2 and C-6), 53.7 (NCH), 108.1 (C=CMe), 120.9 and 121.0 (C-4'), 121.7 (C-7'), 123.7 and 124.0 (C-6'), 126.0 (C-5'), 135.4 and 135.5 (C-7a'), 155.4 and 155.7 (C-3a'), 166.3 (C=CMe), and 172.3 and 176.2 (C-2').

Reaction of MBTS with Acetone

MBTS (664 mg, 2 mmol) and acetone (5.08 g) were stirred at room temperature for 67 h. The solid (634 mg) was filtered off and the solvent evaporated from the filtrate. The filtered solid and the residue (13 mg) from the filtrate were both MBTS by t.l.c.

Reaction of CBS with Acetone

A solution of CBS (1.32 g, 5 mmol) in acetone (60 cm^3) was stirred at room temperature for 24 h with exclusion of light. (The product **2** is sensitive to light: when exposed, it turns yellow.) The precipitate (308 mg) was filtered off and recrystallised from acetone. This was the enamine (**2**) and was identical (by i.r. spectroscopy) with samples obtained previously. The filtrate of the reaction mixture was reduced to ca. 10 cm^3 and cooled in the refrigerator (0°C) to precipitate more of **2** (46 mg). Repeating this process yielded a third crop of **2** (23 mg). The solvent was evaporated from the final filtrate. The residue was dissolved in diethyl ether (30 cm^3) and extracted with aqueous sodium dihydrogen phosphate, dihydrate (0.1M, $3 \times 30\text{ cm}^3$), and

then with aqueous sodium hydroxide (2.5 *M*, 3 × 15 cm³). The pH of the combined sodium dihydrogen phosphate extracts was adjusted to 12 with aqueous sodium hydroxide (2.5*M*) and the ketone (**1**) (30 mg) (identified by i.r. spectroscopy) filtered off. Benzoyl chloride (2 cm³) was added to the filtrate and the mixture shaken for 10 min. This gave *N*-cyclohexylbenzamide (313 mg, 31%), which was filtered off and recrystallised from aqueous ethanol giving 221 mg (22%), m.p. 146.1°C–148.4°C (Reference 4, m.p. 147°C); the i.r. spectrum was identical to that of an authentic sample prepared from cyclohexylamine, benzoyl chloride and aqueous NaOH. The combined sodium hydroxide extracts were acidified with hydrochloric acid (2*M*). MBT (12 mg, 1.4%) was filtered off; the i.r. spectrum was identical to a reference spectrum. The solvent was evaporated from the ethereal solution and the residue eluted with dichloromethane on a silica gel column. The first fraction was the ketone (**1**) (403 mg, total yield 433 mg, 39%), which was recrystallised from petroleum ether (b.p. 40°C–60°C) and was identical (by i.r. spectroscopy) to samples obtained previously. The next fraction was triturated with petroleum ether (b.p. 40°C–60°C yielding more **2** (8 mg, total yield 385 mg, 33%).

This reaction was carried out several times. On the other occasions, similar amounts of **2** and higher yields (up to 62%) of **1** were obtained, but yields of MBT and cyclohexylamine (as its benzamide) were not determined.

Reaction of 2'-benzothiazolylthiopropan-2-one (**1**) with CBS

In the presence of cyclohexylamine. CBS (2.64 g, 10.0 mmol) dissolved in diethyl ether (225 cm³), **1** (2.24 g, 10.0 mmol) in diethyl ether (70 cm³), and cyclohexylamine (0.997 g, 10.05 mmol) were combined together and stirred at room temperature in the dark. After six days, the precipitate was filtered off. By ¹H NMR spectroscopy, this was a mixture of the enamine (**2**) (2.87 g) and 1,1-bis-(2'-benzothiazolylthio)-propan-2-one (**4**) (1.07 g, 28%). These were separated by eluting

on a silica gel column with dichloromethane. **4** (0.53 g, 14%) eluted first and was recrystallised from petroleum ether (40°C–60°C), m.p. 87.0°C–87.7°C (Found: C, 52.5; H, 3.1; N, 7.4. C₁₇H₁₂N₂OS₄ requires C, 52.6; H, 3.1; N, 7.2%); ν_{\max} (KBr) 1735(CO), 1460, 1430, 995 and 755 cm⁻¹; δ_{H} (90 MHz; CDCl₃) 2.59 (3H, s, CH₃), 6.68 (1H, s, CH), 7.1–7.5 (4H, m, 5'-H and 6'-H) and 7.6–7.9 (4H, m, 4'-H and 7'-H). **2** (2.72 g, 58%) eluted later and was recrystallised from acetone, m.p. 201.8°C–202.5°C; i.r. and ¹H NMR spectra were identical with those of earlier samples.

The filtrate from the reaction mixture was reduced to 30 cm³ and extracted successively with aqueous sodium dihydrogen phosphate, dihydrate (1*M*, 3 × 30 cm³), aqueous sodium hydroxide (1*M*, 3 × 15 cm³) and water (3 × 10 cm³). The phosphate extracts were combined and their pH adjusted to 11.5 with aqueous sodium hydroxide (1*M*). Benzoyl chloride (4 cm³) was added to this in 1 cm³ portions and the mixture shaken for 10 min. *N*-cyclohexylbenzamide (2.26 g) was filtered off (i.r. spectrum was identical with that of an authentic sample). The combined sodium hydroxide extracts were acidified with hydrochloric acid (2*M*). MBT (0.7 mg, 0.04%) was filtered off. During extraction, a precipitate appeared in the ethereal layer. This was filtered off and shown by ¹H NMR spectroscopy and t.l.c. to be **2** (109 mg). More **2** (17 mg) precipitated from the new filtrate on standing. After filtering this off, the ether was evaporated and the residue eluted on a silica gel column with dichloromethane. The first main fraction was unreacted CBS (59 mg, 2.2%). The last fraction collected was **2** (36 mg, total yield 65%, or 66% based on CBS consumed).

The intermediate fractions were rechromatographed on silica gel eluting with dichloromethane/petroleum ether (b.p. 40°C–60°C) (50:50). The first main fraction was unreacted **1** (31 mg, 1.4%). Next was 1,3-bis-(2'-benzothiazolylthio)propan-2-one (**3**) (165 mg, 4.2%, or 4.3% based on CBS consumed), which was recrystallised from cyclohexane, m.p. 127.9°C–128.0°C

(Reference 6, m.p. 127°C) (Found: C, 52.7; H, 3.3; N, 7.1. Calculated for $C_{17}H_{12}N_2OS_4$: C, 52.6; H, 3.1; N, 7.2%); ν_{max} (KBr) 2940, 2895, 1730(CO), 1460, 1425, 1000 and 755 cm^{-1} ; δ_H (400 MHz; $CDCl_3$) 4.50 (4H, s, CH_2), 7.30 (2H, ddd, J 1.2, 7 and 8 Hz, 5'-H or 6'-H) 7.40 (2H, ddd, J 1.3, 7 and 8 Hz, 5'-H or 6'-H), and 7.75 and 7.82 (4H, 2xd, J 8 Hz, 4'-H and 7'-H).

In the absence of cyclohexylamine. CBS (132.5 mg, 0.50 mmol) in diethyl ether (30 cm^3) and **1** (111.6 mg, 0.50 mmol) were stirred together at room temperature in the dark for fourteen days. The precipitate was filtered off. By 1H NMR spectroscopy, this was a mixture of **2** (113.3 mg) and **4** (24.1 mg, 12%), which can be separated by eluting with CH_2Cl_2 on silica gel as described above. The solvent was evaporated from the filtrate from the reaction mixture and the residue subjected to preparative t.l.c. on silica gel eluting seven times with CH_2Cl_2 . Fraction 4 was **3** (14.5 mg, 4.3%). Fraction 6 was recrystallised from chloroform yielding MBT (0.7 mg, 0.8%), m.p. 181.5°C–181.9°C (Reference 4, m.p. 177°C–179°C). Fraction 8 was **2** (14.1 mg, total yield 127.1 mg, 54%).

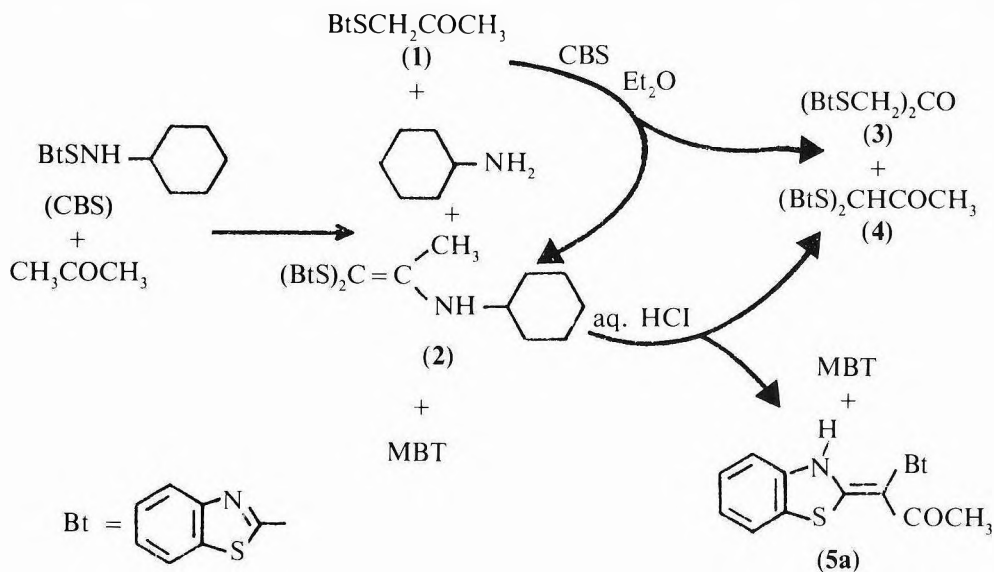
Hydrolysis of **1**, 1-bis-(2'-benzothiazolylthio)-2-cyclohexyl-aminoprop-1-ene (**2**)

A solution of the enamine (**2**) (940 mg, 2 mmol) in dichloromethane (150 cm^3) was stirred with hydrochloric acid (2*M*, 50 cm^3) initially at room temperature for eleven days and then under reflux for 117 h. The organic layer was washed with aqueous saturated sodium bicarbonate (75 cm^3) and water (2 × 75 cm^3), and dried ($MgSO_4$). The solvent was evaporated and the residue eluted on a silica gel column with dichloromethane. The sixth fraction was the ketone (**4**) (380 mg, 49%), which was recrystallised from petroleum ether (b.p. 40°C–60°C), m.p. 84.6°C–85.0°C, the i.r. spectrum was identical to that of the sample obtained above. The seventh fraction was MBT (60 mg, 9%) and was recrystallised from chloroform, m.p. 179.2°C–181.3°C (Reference 4, 177°C–179°C), i.r. and NMR spectra were identical with reference spectra. The eighth fraction was (E)-1-2'-benzothia-

zoyl-1-2' (3' H)-benzothiazolylidene-2-propanone (**5a**) (40 mg, 6%), which was recrystallised twice from cyclohexane and then twice from ethanol, m.p. 187.9°C–188.4°C (Reference 7, m.p. 185°C) (Found: C, 62.8; H, 3.9; N, 8.5. $C_{17}H_{12}N_2OS_2$ requires C, 62.9; H, 3.7; N, 8.6%); ν_{max} (KBr) 3430 (NH), 1605, 1500, 1455, 1435, 1375 and 740 cm^{-1} ; λ_{max} (EtOH) 365 nm; δ_H (300 MHz; $CDCl_3$) 2.81 (3H, s, CH_3), 7.33 and 7.49 (4H, 2xt, J 7 Hz, 5'-H and 6'-H), 7.77 and 7.82 (4H, 2xd, J 8 Hz, 4'-H and 7'-H), and 16.05 (1H, s, OH). In $CDCl_3$, this contained 14% of a mixture of the tautomers (**5b** and **5c**); δ_H (300 MHz) 2.63 (3H, s, CH_3), 7.4 (4H, 2xt, 5'-H and 6'-H), 7.61, 7.74, 7.88 and 8.05 (4H, 4xd, J 8 Hz, 4'-H and 7'-H), and 15.87 (1H, s, NH or OH). Small quantities of several other products were also obtained from the column, but they were insufficient for full characterisation.

RESULTS AND DISCUSSION

No reaction was detected between MBTS and acetone after 67 h at room temperature, although MBTS is fairly insoluble in acetone at room temperature and only about 2% was in solution. On the other hand, CBS which is more soluble, reacted readily with acetone and all had reacted after about 24 h at room temperature. Two main products were obtained. One (**2**) precipitated out of the reaction mixture in a yield of 33%. Its 1H and ^{13}C NMR spectra revealed the presence of two benzothiazole groups, a methyl and a cyclohexylamino group. In the ^{13}C spectrum, most of the benzothiazole carbons appear as doublets implying that the two groups have slightly different environments; two additional downfield resonances are also present. The i.r. spectrum confirmed the presence of the amino and benzothiazol-2-ylthio groups, and a u.v. absorption at 226 nm is also consistent with two substituted benzothiazolyl groups. The proposed structure (**2**) was eventually established by elemental analysis. The other main product was identified as the ketone (**1**) and was isolated by column chromatography in yields of up to 62%. Also produced were cyclohexylamine and a trace (1.4%) of MBT (isolated as such but presumably present in the



product mixture as its cyclohexylammonium salt). The cyclohexylamine was isolated as its benzoyl derivative (31%).

It would seem likely that the ketone (1) is an intermediate in the formation of the enamine (2) from CBS. To confirm this, the reaction of 1 with CBS in the absence of acetone was investigated. Instead of acetone, an inert solvent, diethyl ether, was used. The reaction took two weeks to go to completion, but as predicted 2 was obtained in 54% yield together with a trace (0.8%) of MBT and two other minor products. These were characterised as 1,3-bis-(2'-benzothiazolylthio) propan-2-one (3)⁶ and 1,1-bis-(2'-benzothiazolylthio) propan-2-one. As mentioned above, cyclohexylamine is a by-product of the reaction of CBS and acetone. It was found to catalyse the reaction of 1 with CBS, although complete reaction still took six days. 2 (66%), 3 (4.3%), 4 (28%) and MBT (0.04%) were all isolated.

3 and 4 were not originally detected in the reaction between CBS and acetone. On re-investigation, a trace (0.3%) of 3 was found. 4 was not found, but as 2 and 4 have apparently identical retention on silica gel, a trace of 4 in the reaction would be difficult to detect. At least part of the explanation for the significant yield of 4 from the reaction between CBS and

1 in diethyl ether may be solubility. Both 2 and 4 are virtually insoluble in diethyl ether and would precipitate out when formed. In contrast, in acetone, 2 is also insoluble while 4 is soluble, thus an equilibrium between 2 and 4 would favour 2 in acetone.

To provide further confirmation for the proposed structure (2), the enamine was hydrolysed with aqueous hydrochloric acid. The hydrolysis was slow, but the expected product (4) was obtained in 49% yield. A large number of minor by-products were also obtained. Two were identified: one was MBT (9%) and the other was characterised as (*E*)-1-2'-benzothiazolyl-1-2' (3'*H*)-benzothiazolylidene-2-propanone (5a). The unexpected absence of benzothiazolylthio groups in the latter was indicated by the lack of a characteristic C-S i.r. absorption at about 1000 cm^{-1} , and confirmed by the elemental analysis. This compound (5a) has been obtained previously⁷, but was assigned the (*Z*)-tautomeric structure (5c). The present assignment [predominantly the (*E*)-tautomer (5a)] is based on NMR spectroscopy in various solvents (Table 1).

In CDCl_3 , two sets of signals in the ratio 86:14 are visible. In the major group, the corresponding protons of the two benzothiazole

TABLE I. ^1H NMR SPECTRAL SIGNALS OF 5δ (p.p.m.)

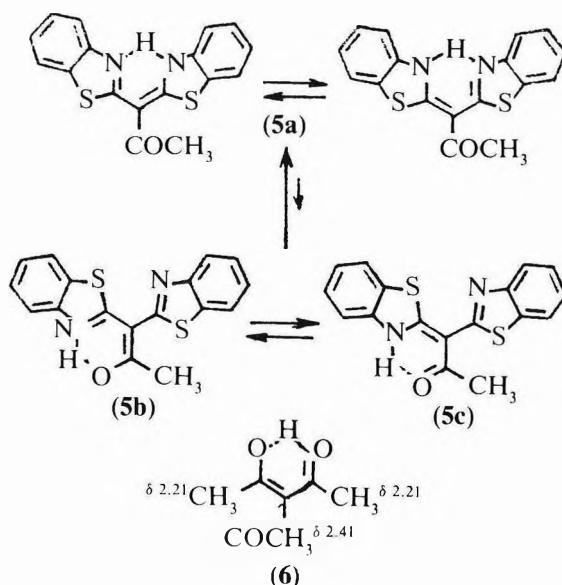
Solvent	CH_3		5-H, 6-H		4-H, 7-H		OH/NH	
	5a	5b/5c	5a	5b/5c	5a	5b/5c	5a	5b/5c
$(\text{CD}_3)_2\text{SO}$	2.60	-	7.38	7.54	8.04	-	14.87	-
$(\text{CD}_3)_2\text{CO}$	2.74	-	7.40	7.55	8.01	-	15.89	-
CDCl_3	2.81	2.63	7.33	7.49	7.77, 7.82	7.61, 7.74, 7.88, 8.05	16.05	15.87
CD_2Cl_2	2.79	2.64	7.35	7.51	7.83, 7.86	7.67, 7.81, 7.92, 8.03	16.02	a
C_6D_6	2.64	2.45	6.94	7.11	7.31, 7.36	S, S, 7.51, 8.17	a	a

S Submerged under other signals

a Not observed

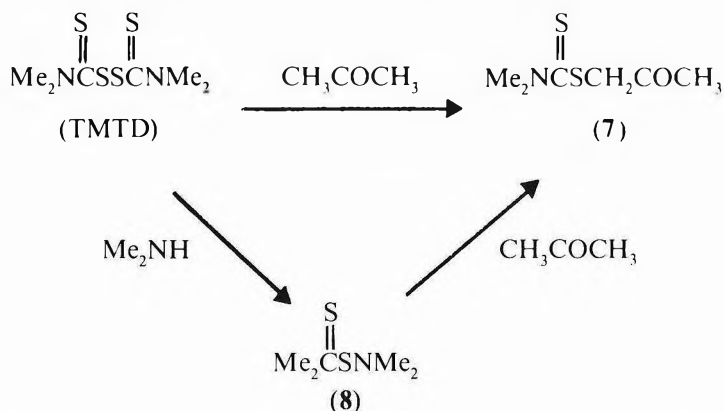
groups are equivalent, while in the minor group, the protons at the 4- and 7- positions are not equivalent. In more polar solvents (CD_3COCD_3 and CD_3SOCD_3), the minor signals disappear, whereas in the less polar CD_2Cl_2 and C_6D_6 , their contributions increase to 15% and 23%, respectively. Proton transfer between the nitrogens in 5a would be expected to be fast on the NMR time scale leading to equivalence of the benzothiazole groups. Proton transfer between oxygen and nitrogen in the equilibrium of 5b and 5c should also be fast but here the benzothiazole groups will retain their non-equivalence. Consequently, the major NMR signals are assigned to the (*E*-

tautomer (5a), and the minor signals appearing in the less polar solvents to an equilibrium of 5b and 5c. These assignments are supported by the chemical shifts of the methyl groups. Based on the spectrum of triacetylmethane (6), the protons of the acetyl group in 5a would be expected to be shifted downfield from those of the hydrogen-bonded acetyl/enol groups in 5b/5c. The effect of solvent polarity on the tautomeric equilibria suggests that there is a significant content of 5b in the 5b/5c equilibrium, as 5b would probably have the least contribution from zwitterionic canonical forms of the three tautomers.



As mentioned in the introduction, Jefferson *et al.*³ have observed previously that TMTD undergoes a reaction similar to the formation of **1** from CBS. The ketone (7) is produced from TMTD after four days at room temperature, which is a little slower than the formation of **1** from CBS. However, they found that the sulphenamide (8) reacts very

rapidly with acetone, the reaction taking only 10 min at room temperature. This suggests that TMTD itself reacts with acetone *via* the sulphenamide (8), as any dimethylamine, present as an impurity or produced from TMTD, would readily lead to the formation of 8 which in turn would rapidly react with acetone regenerating the amine.



CONCLUSIONS

CBS has been found to react with acetone at room temperature to give the ketone (1), the enamine (2), cyclohexylamine and a trace of MBT. 2 was shown to be produced *via* 1. Based on this and previous work³, the order of reactivity of different types of accelerator towards acetone appears to be MBTS < thiuram disulphides < benzothiazolesulphenamides < thiocarbamoylsulphenamides. This reactivity should be borne in mind when employing acetone extraction in the analysis of curatives in rubber compounds or vulcanisates.

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Accelerated Long-term Ageing of Natural Rubber Vulcanisates Part 2: Results from Ageing Tests at 40°C

L. R. BARKER*

Studies of the influence of temperature on oven-ageing performance of black-filled natural rubber compounds vulcanised with conventional, semi-EV, EV and mixed Novor/sulphur curing systems have continued with testing at 40°C. With conventional and semi-EV vulcanisates, it was confirmed that the time to 80% retention of tensile strength followed an Arrhenius-type relationship but performance was above expectation for the EV compound. After five years at 40°C, tensile strength of the Novor/sulphur compound was still more than 80% of the unaged value as would be expected from ageing tests at higher temperatures. This compound also showed a tendency to increased modulus and longer fatigue life after ageing at 40°C as has been observed at higher ageing temperatures.

Studies of the influence of temperature on oven-ageing performance of black-filled natural rubber compounds vulcanised with conventional, semi-EV, EV and mixed Novor/sulphur curing systems were published in 1987 using

results of tests carried out at 50°C-100°C on formulations given in *Table 1*¹.

It was found that the time to 80% retention of tensile strength during ageing followed an

TABLE 1. FORMULATIONS

Compound	Formulation			
	1	2	3	4
Natural rubber, SMR L	100	100	100	100
N330, HAF black	50	50	50	50
Aromatic process oil	4	4	4	4
Zinc oxide	5	5	5	5
Stearic acid	3	3	3	1
IPPD	2	2	2	-
TMQ	-	-	-	2
ZMBI	-	-	-	1
Sulphur	2.5	1.6	0.25	0.4
CBS	0.5	1.1	-	0.08
MBS	-	-	2.1	-
TMTD	-	-	1.0	-
TMTM	-	-	-	1.3
Novor 924 ^a	-	-	-	4.2

^aUrethane vulcanising agent (Rubber Consultants)

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

Arrhenius-type relationship and changing the ageing temperature had the effect of altering relative resistance to degradation among the test compounds. Modulus changes during ageing were shown to be temperature-dependent and the earlier observations that, for a Novor curing system, ageing at 100°C gave a tendency to a higher tension fatigue life despite an increase in stiffness were confirmed for ageing at 50°C.

Concurrent with this work, but over a longer period, ageing tests at 40°C were also carried out on the same formulations. Apart from oven temperature, there were no changes in the experimental details already described¹.

The effect of ageing at 40°C on performance is of particular interest because this temperature is at the top end of a range that covers normal environmental conditions. Rubber would be expected to reach this temperature quite frequently in hotter parts of the world and in temperate regions, hot spots would be found indoors in areas such as near machinery and space heating systems where conditions are not severe enough to require special elastomers. A demonstration of the ability of accelerated ageing tests to forecast resistance to deterioration down to 40°C would therefore be of considerable practical value.

RESULTS

Effect of Temperature on Ageing

Table 2 is similar to Table 6 in the previous paper¹ but with data from ageing at 40°C incorporated. There are some small changes to Arrhenius slopes for *Formulations 1* and 2, as would be expected, but the low probability levels indicate a considerable improvement in precision. A typical Arrhenius relationship is plotted in *Figure 1*.

It can be seen in *Table 3* that, for *Formulations 3* and 4, tensile strength was not reduced enough by ageing at 40°C to estimate the time to 80% retention. This is understandable for the Novor/sulphur formulation because the estimate from earlier data indicated a time of nearly seven years but results are clearly above expectation for the EV compound.

With *Formulations 1* (15.5 min at 105°C), 2 (10 min at 150°C), 3 and 4 increases in tensile strength were observed after ageing eighty-seven weeks at 40°C. At higher temperatures, data were not obtained at sufficient short times to determine whether similar increases in tensile strength occurred. *Figures 2* and *3* relate to the performance of two compounds to ageing time at 40°C and 70°C. Time scales at the higher temperature have been adjusted according to the Arrhenius relationship using the following equation:

$$D_1/D_2 = \exp [B(10^3/T_1 - 10^3/T_2)] \quad \dots 1$$

where D_1 = ageing time at temperature T_1 (K)
 D_2 = ageing time at temperature T_2 (K)
 B = Arrhenius constant
 $= 10^{-3} \times$ apparent activation energy/gas constant.

Effect of Ageing on Properties

Modulus and hardness. Even a casual examination of M100, M200 and hardness results indicates that, with a few exceptions, ageing at 40°C has generally increased stiffness over that at 50°C. This can be seen more clearly in *Figure 4* where percentage retentions of M100 for all the formulations are plotted against time of ageing at 40°C and 50°C with the time scales for the former temperature modified according to *Equation 1*. It can also be seen that increases in percentage retention are lower for the low sulphur formulations and for the shorter cure times with the conventional and semi-EV compounds relative to their overcures.

Compression set and resilience. Unstrained ageing of compression set test-pieces is probably not very informative for estimating performance in the deformed state but may be of some value for indicating the shelf-life of a component before being put into service. With three of the formulations, there were improvements in compression set after ageing at 40°C. Although ageing had less effect on the conventional compound when overcured, this did not compensate for the inferior unaged compression set.

TABLE 2. TIME OF AGEING TO 80% RETENTION OF TENSILE STRENGTH

Item	Formulation					
	1	2	3	4	5	6
Cure time, 150°C (min)	15.5	93	10	60	16	15
Experimental values (days)						
100°C	1.0	1.8	2.8	2.6	5.8	4.6
70°C	23	30	40	44	66	92
50°C	290	210	480	340	600	700
40°C	1 316	938	1 960	1 022	-	-
Regression estimates ^a (days, versus 1/T)						
100°C (days)	0.949 (0.982)	1.77 (1.87)	2.48 (2.61)	2.70 (2.66)	- (5.50)	- (4.82)
40°C (years)	3.3 (3.0)	2.2 (1.9)	4.8 (4.1)	2.9 (3.1)	- (4.6)	- (6.8)
Regression analysis Slope × 10 ⁻³ (B)	13.92 (13.65)	11.95 (11.49)	12.75 (12.35)	11.63 (11.76)	- (11.14)	- (12.14)
Intercept	-37.4 (-36.6)	-31.5 (-30.2)	-33.3 (-32.1)	-30.2 (-30.5)	- (-28.2)	- (-31.0)
Correlation coefficient	0.9997 (0.9999)	0.9988 (0.9995)	0.9985 (0.9985)	0.9998 (0.9998)	- (0.9990)	- (0.9993)
t	57.3 (79.5)	29.0 (32.0)	26.0 (18.5)	75.6 (52.9)	- (21.9)	- (27.0)
Probability level (%)	0.03 (0.8)	0.12 (2.0)	0.15 (3.4)	0.02 (1.2)	- (2.9)	- (2.4)

^a Figures within brackets are estimated from results obtained at ageing temperatures 50°C, 70°C and 100°C only.

Increases in resilience observed for the EV compound are consistent with those found at higher ageing temperatures and probably

indicate post-cure crosslink maturation. This effect should be minimised by vulcanising for a longer period. For the other formulations,

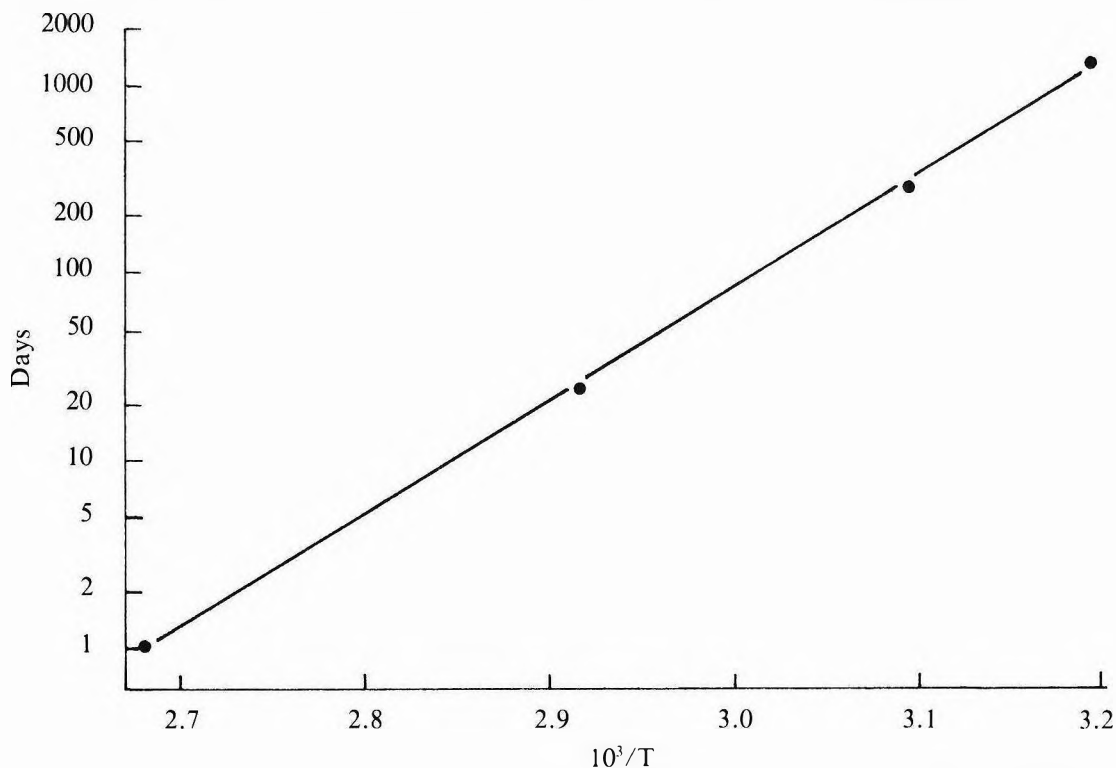


Figure 1. Arrhenius plot of ageing time to 80% retention of tensile strength, Formulation 1, cure 15.5 min at 150°C.

changes in resilience during ageing at 40°C were negligible.

Tension fatigue. Fatigue lives after ageing at 40°C might be expected to be lower than those at 50°C due to increased modulus but this is not evident in the results. Once again a positive change in fatigue performance was seen with the Novor/sulphur compound.

Ageing at 23°C. Over the period that ageing at 40°C was in progress, test-pieces were also stored at 23°C in the controlled atmosphere of a physical testing laboratory and results from these are included in Table 3. Storage time was equivalent to twenty to thirty-four weeks at 40°C and this mild severity of ageing is reflected in relatively lower changes in modulus and hardness. Further ageing at 23°C would be expected to lead to greater increases in stiffness. For similar reasons, changes in

tensile strength and elongation at break were comparatively small with, in some instances, increases in values as seen with 40°C ageing.

High retention of fatigue life had the effect that conventional and semi-EV compounds still gave a better performance than those with EV or Novor/sulphur curing systems after five years at 23°C.

DISCUSSION

It is now well established that there are a number of chemical reactions that occur in rubber during ageing that lead to both molecular break-down and crosslinking. Each of these reactions proceeds at its own rate which is independently influenced by temperature. Results from these studies suggest that at high ageing temperatures network break-down leading to loss of strength tends to have the

TABLE 3. PERCENTAGE RETENTION OF PROPERTIES AFTER AGEING

Property	Formulation					
	1	2	3	4	5	6
Cure time, 150°C (min)	15.5	93	10	60	16	15
Ageing conditions						
M100						
40°C, 87 weeks	196	261	174	184	160	177
40°C, 174 weeks	267	282	186	214	163	166
40°C, 261 weeks	251	337	205	214	171	171
23°C, 261 weeks	174	155	122	139	130	140
M200						
40°C, 87 weeks	184	235	156	161	150	150
40°C, 174 weeks	212	232	154	172	145	140
40°C, 261 weeks	207	-	165	173	149	138
23°C, 261 weeks	154	136	111	123	120	122
Tensile strength						
40°C, 87 weeks	103	95	105	93	108	107
40°C, 174 weeks	84	69	86	75	95	93
40°C, 261 weeks	72	60	82	66	91	86
23°C, 261 weeks	105	91	95	97	107	102
Elongation at break						
40°C, 87 weeks	75	58	81	69	87	87
40°C, 174 weeks	57	43	74	45	85	76
40°C, 261 weeks	49	33	65	48	82	76
23°C, 261 weeks	95	84	94	92	104	98

TABLE 3. PERCENTAGE RETENTION OF PROPERTIES AFTER AGEING (Contd.)

Property	Formulation					
	1	2	3	4	5	6
Cure time, 150°C (min)	15.5	93	10	60	16	15
Ageing conditions						
Hardness						
40°C, 87 weeks	113	122	113	110	116	106
40°C, 174 weeks	116	127	115	116	113	105
40°C, 261 weeks	121	128	116	118	116	102
23°C, 261 weeks	109	114	109	106	104	101
Resilience						
40°C, 87 weeks	101	102	101	101	109	-
40°C, 174 weeks	98	99	101	97	111	102
40°C, 261 weeks	100	102	102	98	110	100
23°C, 261 weeks	95	98	100	98	105	105
Compression set						
40°C, 87 weeks	111	92	91	100	70	78
40°C, 174 weeks	111	100	82	109	70	83
40°C, 261 weeks	111	92	91	118	70	89
23°C, 261 weeks	100	108	100	127	90	89
Fatigue life						
40°C, 87 weeks	37	40	55	83	74	119
40°C, 174 weeks	15	5	30	23	69	110
40°C, 261 weeks	6	0	23	8	50	106
23°C, 261 weeks	85	81	75	98	90	80

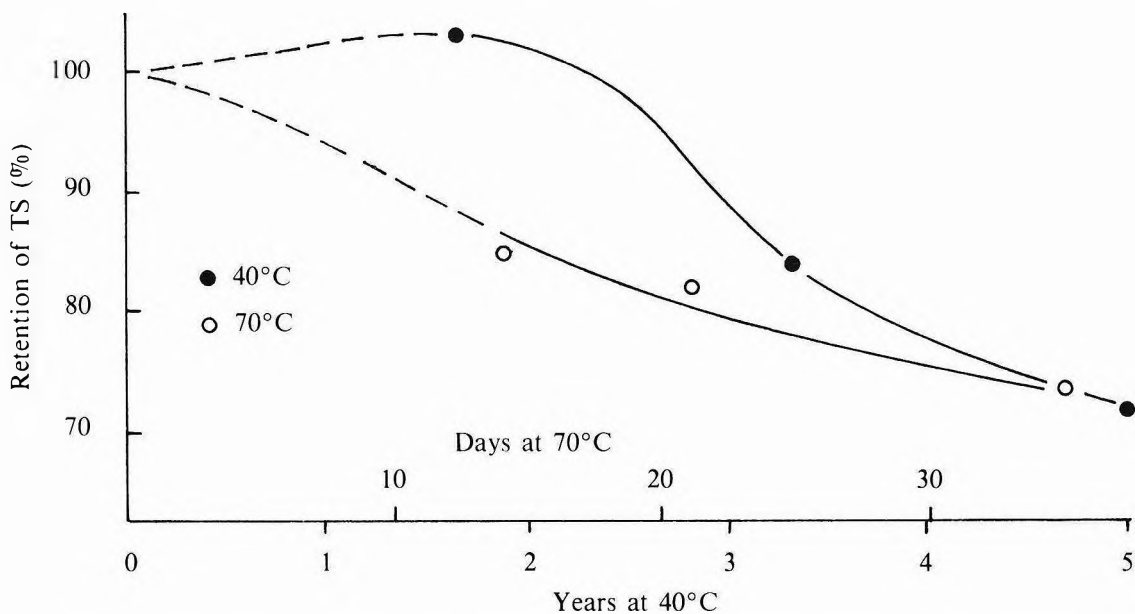


Figure 2. Percentage retention of tensile strength versus time of ageing at 40°C and 70°C, Formula 1, cure 15.5 min at 150°C.

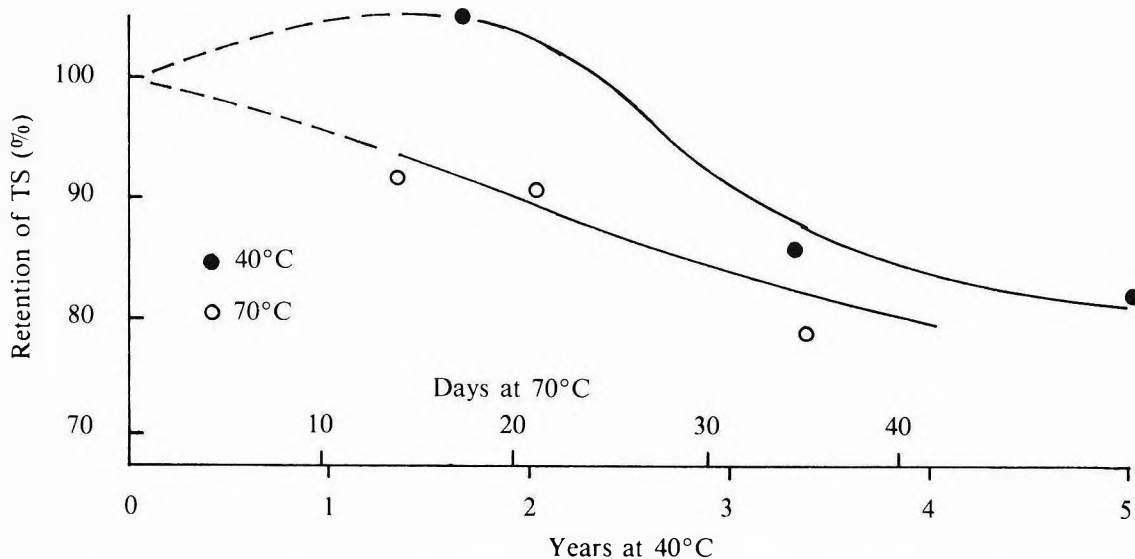


Figure 3. Percentage retention of tensile strength versus time of ageing at 40°C and 70°C, Formulation 2, cure 10 min at 150°C.

dominant influence while at lower temperatures crosslinking is relatively more important and can partly compensate for the effect of

degradation. The difference in the net effect of these reactions at 40°C and 70°C can clearly be seen in Figures 2 and 3 for conventional and

Ageing times at 40°C have been transposed to equivalent times at 50°C in accordance with Equation 1.

- A Formulation 1, cure 15.5 min at 150°C
- B Formulation 1, cure 93 min at 150°C
- C Formulation 2, cure 10 min at 150°C
- D Formulation 2, cure 60 min at 150°C
- E Formulation 3, cure 16 min at 150°C
- F Formulation 4, cure 15 min at 150°C

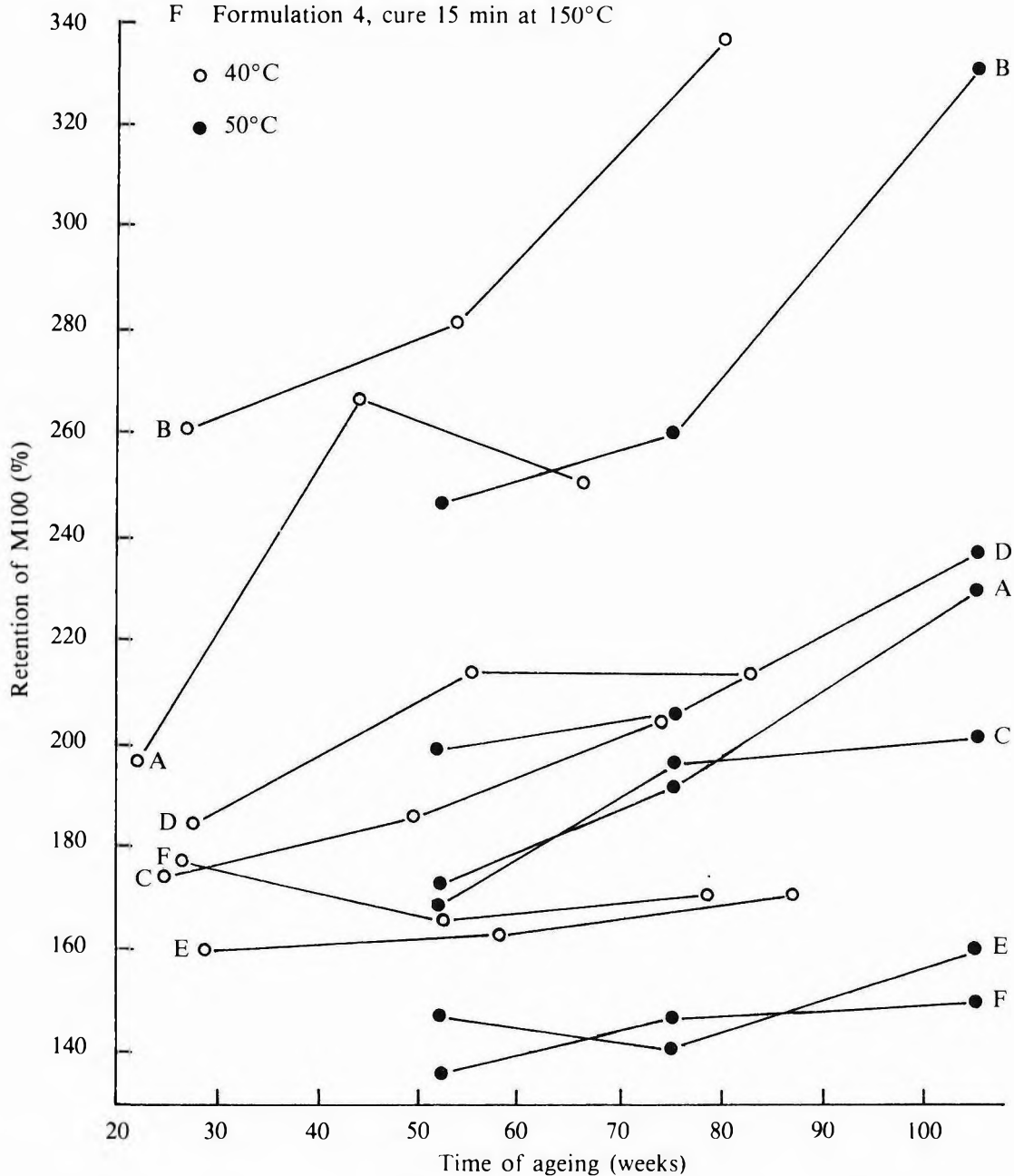


Figure 4. Retention of M100 versus time of ageing at 40°C and 50°C.

semi-EV curing systems and it is fortuitous that times to 80% retention of tensile strength at 40°C agree so well with predictions made from higher temperature results by the use of the Arrhenius expression. It seems likely that such predictions would break down for lower ageing temperatures as has happened at 40°C with the EV formulation.

CONCLUSIONS

Ageing tests at various temperatures have emphasised the complex nature of oxidative deterioration and the limitations of standard methods of assessment when the positive effects of crosslinking occur simultaneously with network degradation. With the conventional and semi-EV formulations used in this work, estimates of ageing by the Arrhenius method can be made with a reasonable degree of confidence down to 40°C but there is a risk of under-estimating ageing resistance at this temperature with the EV compound. Fortunately, this is a fail-safe situation:

projections of ageing behaviour to below 40°C from results obtained at higher temperatures are likely to be pessimistic relative to performance in service.

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REFERENCE

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Comparison of Free Fatty Acid Values with Individually Determined Organic and Inorganic Acid Concentrations in the Extracts of Malaysian Natural Rubber

R.C. CRAFTS,* J.E. DAVEY,* G.P. McSWEENEY* AND I.S. STEPHENS*

Free fatty acid (FFA) values are frequently taken to be a measure of the long-chain fatty acid content of rubber samples. However, from an analytical view-point, it is apparent that the acidity measured during this test could not be due, entirely, to acids containing more than ten carbon atoms. Ion chromatography and gas chromatography have been used to identify and quantify the acidic components of the acetone extract of natural rubber. The combined acid concentrations measured by these techniques account for more than 85% of the FFA value and, of this figure, low molecular weight organic and inorganic acids account for up to one half. It may be concluded that expressing the result of an FFA titration as 'stearic acid' can seriously over-estimate the quantity of long-chain fatty acids present in natural rubber and may mask important differences in the composition of both these and the low molecular weight materials.

The 'free fatty acid' (FFA) value, as normally expressed, is the number of milligrammes of stearic acid equivalent to the amount of potassium hydroxide required to neutralise the acetone extract from 5 g of rubber and this has, for many years, been taken as a criterion of rubber quality because of its degree of correlation with cure rate and processability¹.

Historically, the FFA value has always been reported as stearic acid, even though it has been well known that other long-chain saturated and unsaturated fatty acids such as lauric, palmitic, oleic, linoleic and linolenic acids are present. This fact alone produces some degree of error and the intention of this study is to investigate the extent to which this error is compounded by the presence of low molecular weight acids in the extract of NR.

The total acid contents of the rubber samples were estimated by alkali titration of acetone extracts, long-chain fatty acids were estimated by gas chromatography (GC) after methylation

and the low molecular weight anions, both organic and inorganic, were estimated by ion chromatography (IC).

REAGENTS AND APPARATUS

Reagents

The reagents were used as received, without further purification. These include heptadecanoic acid (Sigma, 99%), methanolic boron trifluoride (BDH, 14%), heptane (BDH, HiPerSolv), sodium chloride (BDH, Analar), acetone (BDH, Analar), propan-2-ol (BDH, Analar), sodium carbonate (BDH, Aristar), potassium hydrogen carbonate (BDH, Analar), 0.1 M sodium hydroxide (BDH, concentrated volumetric solution), acetonitrile (FSA Laboratory Supplies, HPLC grade), 0.5M sulphuric acid (BDH, Analar volumetric solution) and indicators - bromothymol blue (BDH) and phenolphthalein (BDH) both prepared as 0.05% solutions in absolute ethanol (BDH, Analar).

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

Apparatus

The equipment used consisted of: Perkin Elmer F17 GC with a flame ionisation detector; JJ's (Chromatography) Ltd 3mm × 4m packed column of 20% diethylene glycol succinate (DEGS) on Chrom. W; Trilab II computing integrator; Baird and Tatlock rotary evaporator; Gallenkamp water-bath; Dionex model 2000i IC with conductivity detector; Dionex HPIC-AG4 guard column, HPIC-AS4 and HPICE-AS1 separator columns and HSC chloride suppressor column; Dionex AFSI suppressor fibres.

EXPERIMENTAL

Samples were supplied from Malaysia as dried latex taken from trees of clone PB 28/59. The dried rubber was prepared by pouring the latex onto glass-fibre filter discs and then drying in *vacuo* at ambient temperature to constant weight. Any preservatives added to the latex prior to drying, the quantity of latex applied to each disc and other variations in the procedure are detailed below for each sample.

Sample 1. Field latex 32% dry rubber content (d.r.c.), 1% volume/volume of 20% weight/volume ammonia solution was added (nominal 0.2% weight/volume NH₃) as a preservative. 10 ml of latex was poured onto each disc within 1 h of ammoniation. The sample was extracted five days after collection.

Sample 2. Unammoniated fresh field latex 38.7% d.r.c., no preservatives were added, 13 ml of latex was poured onto each disc. The drying was started about 5 h after tapping commenced. The sample was extracted five days after collection.

Sample 3. Field latex, 44.8% d.r.c., 20 ml of latex was poured onto each disc. The sample was extracted twelve days after collection.

Sample 4. Field latex. The sample was extracted four days after collection.

Sample 5. Field latex collected into 10% aqueous sodium fluoride in ice-cooled

containers. The sample was extracted three days after collection.

Sample 6. Field latex. The sample was extracted five days after collection.

Sample 7. Field latex collected in an ice-cooled container. The dried discs were extracted five days after collection.

Although conventional² FFA determinations are carried out on the acetone extract of rubber, this was not ideal in the context of this study and, for two reasons, propan-2-ol was the preferred extractant. Firstly, it avoided the necessity of evaporating the sample before titration, as the titration medium was propan-2-ol/water (80/20); and secondly, the ion chromatograph columns are based on a polystyrene resin which swells in solutions containing even trace levels of acetone causing unacceptable increases in back-pressure and possible column damage.

In order to check the validity of changing the extractant, a series of rubber samples was extracted with both solvents. Two of the samples were dosed with additional stearic acid to test the recovery of fatty acid from the rubber. As shown below, this does not affect the amount of FFA determined by titration (*Table 1*) and the added stearic acid shows

TABLE 1. COMPARISON OF FREE FATTY ACID VALUES FOLLOWING EXTRACTION BY PROPAN-2-OL OR ACETONE

Sample	Percentage FFA as stearic acid	
	Acetone extraction	Propan-2-ol extraction
A	0.98	0.90
B	0.77	0.76
C ^a	7.19	7.19
D	1.50	1.54
E ^b	9.63	9.53

^aSample C was Sample B dosed with 6.5% by weight stearic acid.

^bSample E was Sample D dosed with 8.2% by weight stearic acid.

recovery of over 97% for the two dosed samples with both solvents.

Sample 3 was also subjected to a second extraction some three weeks after the first. Any differences between the two fatty acid profiles were expected to indicate the effect of storage on dried latex fatty acid composition.

The full compositional analyses for *Samples 1-6* are shown in *Tables 2* and *3*.

For *Sample 7*, a completely different procedure was adopted. The sample was sequentially extracted by simply immersing the dried latex in cold propan-2-ol overnight, removing the extracted material, and re-immersing in fresh extractant. The procedure was repeated five times in order to obtain information on whether the hot extraction process was causing hydrolysis of lipids, thereby giving erroneously high results for the fatty acid content. The amount of sample was, unfortunately, insufficient to allow for extraction by both hot Soxhlet and cold immersion. The results for the sequential extractions, denoted by the numbers 7/1 to 7/6, are in *Tables 4* and *5*.

After extraction of the rubber, each extract was diluted to 100 ml with extractant. For the extracts of *Samples 1-6*, the solutions were then split into two equal portions. One portion was taken for GC determination of long-chain fatty acids and the other for titration (to determine total acidity) followed by IC determination for low molecular weight organic and inorganic anions. For the six extracts from *Sample 7*, as no titrations were to be carried out, the solution was split into two unequal parts, 90% being kept for long-chain fatty acid analysis by GC and 10% for the IC determination.

For *Sample 7*, as the cold extracts were expected to extract the same absolute amount of acidic material into six separate extracts, the extracts were not titrated. This enabled the solution to be split into two unequal parts, 90% being kept for long-chain fatty acid analysis by GC and 10% for the IC determination, thereby,

significantly improving the sensitivity for the GC procedure.

Gas Chromatography Determination of Long-chain Fatty Acids

Apart from the addition of an odd carbon-number fatty acid as an internal standard³, samples were prepared according to the AOAC method^{4,5}. The procedure in detail is as follows. Heptadecanoic acid (10 mg accurately weighed) was added to the extract and the solution then evaporated to dryness on a rotary evaporator. A methanolic solution of boron trifluoride (5 ml) was added and the mixture heated under reflux for 5 min. Heptane (3 ml) was then added and the mixture heated under reflux for a further 3-4 min. When the mixture had cooled, saturated salt solution was added and the heptane layer removed for injection into the GC. The carrier gas was nitrogen flowing at 50 ml/min, the column temperature was 190°C and the injection port and detector temperatures 200°C.

Fatty acids were quantified by comparison with the internal standard and correction for relative carbon content of each acid⁶. The retention time of each acid was determined by comparison with a set of standard methyl esters run on the same day as the analyses. The retention time for the furanoic acid⁷ (10, 13-epoxy-11-methyl-octa-decan-10, 12-dienoic acid), was checked by comparison with the methylated extract from a sample of NR known to contain that acid. A typical GC trace of methylated fatty acids is shown in *Figure 1*.

Total Acidity of Titration

For those samples which were extracted with acetone, the extract was evaporated just to dryness on a water-bath, and then re-dissolved in neutral water/propan-2-ol (20/80 volume/volume). Where propan-2-ol was used as the extractant, the alcohol content was adjusted to 80% with water. An indicator, (bromothymol blue or phenolphthalein), was added and standard 0.1M sodium hydroxide used to titrate to the appropriate colour change.

TABLE 2. ANIONS DETERMINED IN LATEX SAMPLES^a
— HOT SOXHLET EXTRACTION

Acid	Sample						
	1	2	3	3 ^b	4	5	6
Lauric	0.06	nd	nd	0.08	0.10	0.07	0.01
Myristic	0.21	0.14	0.22	0.21	0.14	0.12	0.09
Palmitic	2.47	1.99	2.32	2.41	1.48	1.33	0.97
Palmitoleic	0.44	0.30	0.43	0.38	0.29	0.28	0.23
Stearic	4.17	3.25	3.63	3.36	2.55	1.74	1.30
Oleic	3.65	1.28	1.72	1.80	1.70	1.36	0.86
Linoleic	9.00	4.86	5.27	5.10	3.08	2.99	1.82
Linolenic	0.75	0.52	0.53	0.57	0.29	0.30	0.12
Furanoic	3.72	8.22	9.36	6.43	8.38	4.28	5.30
Long-chain acids (m-equiv./kg)	24.48	20.56	23.49	20.35	18.02	12.46	10.69
Hydrochloric	4.43	nd	nd	0.67	0.68	1.02	nd
Glycero-1-phosphoric	0.53	nd	0.32	0.42	0.03	0.21	nd
Glycero-2-phosphoric	nd	nd	nd	nd	nd	0.02	nd
Phosphoric	nd	nd	0.22	0.08	0.09	0.06	0.03
Succinic	0.47	nd	2.44	3.43	0.23	0.06	0.01
Malic	1.98	nd	nd	1.67	0.79	0.24	0.05
Sulphuric	0.19	nd	0.31	0.41	0.05	0.05	0.04
Oxalic	0.12	nd	0.28	0.02	0.10	0.10	nd
Citric	nd	nd	nd	nd	0.08	0.05	0.30
Lactic	3.96	0.71	nd	nd	2.34	0.51	nd
Formic	nd	nd	7.23	0.87	0.34	0.41	0.10
Acetic	3.53	nd	0.62	0.54	0.68	0.78	0.40
Propionic	7.08	nd	0.88	32.51	10.21	5.56	0.57
Inorganic/volatile ^c acids (m-equiv./kg)	25.58	0.71	16.09	46.76	17.19	9.95	2.26

^a Expressed as millimoles of acid per kilogramme of dry rubber from which the anions were extracted

^b This portion of Sample 3 was analysed 21 days after the first portion.

^c The total acid strength for the inorganic and volatile acids has been calculated allowing for the varying basicities of the different acids.

'nd' indicates that the anion was not detected in that sample.

TABLE 3. ANIONS DETERMINED IN EACH SAMPLE EXPRESSED AS A PERCENTAGE OF THE TOTAL ACIDS DETERMINED BY GAS AND ION CHROMATOGRAPHY
— HOT SOXHLET EXTRACTION

Acid	Sample						
	1	2	3	3 ^a	4	5	6
Lauric	0.1	nd	nd	0.1	0.3	0.3	0.1
Myristic	0.4	0.6	0.6	0.3	0.4	0.6	0.7
Palmitic	4.9	9.3	5.9	3.6	4.2	5.9	7.5
Palmitoleic	0.9	1.4	1.1	0.6	0.8	1.2	1.8
Stearic	8.3	15.3	9.2	5.0	7.2	7.7	10.0
Oleic	7.3	6.0	4.3	2.7	4.8	6.1	6.6
Linoleic	18.0	22.9	13.3	7.6	8.8	13.3	14.0
Linolenic	1.5	2.4	1.3	0.8	0.8	1.3	0.9
Furanoic	7.4	38.6	23.7	9.6	23.8	19.1	40.9
Total long-chain acids as % of all acids	48.9	96.7	59.3	30.3	51.2	55.6	82.5
Hydrochloric	8.8	nd	nd	1.0	1.9	4.6	nd
Glycero-1-phosphoric	2.1	nd	1.6	1.3	0.2	1.9	nd
Glycero-2-phosphoric	nd	nd	nd	nd	nd	0.2	nd
Phosphoric	nd	nd	1.7	0.4	0.8	0.7	0.7
Succinic	1.9	nd	12.3	10.2	1.3	0.5	0.2
Malic	7.9	nd	nd	5.0	4.5	2.1	0.8
Sulphuric	0.8	nd	1.6	1.2	0.3	0.4	0.7
Oxalic	0.5	nd	1.4	0.1	0.6	0.9	nd
Citric	nd	nd	nd	nd	0.7	0.7	6.9
Lactic	7.9	3.3	nd	nd	6.6	2.3	nd
Formic	nd	nd	18.3	1.3	1.0	1.8	0.8
Acetic	7.1	nd	1.6	0.8	1.9	3.5	3.1
Propionic	14.1	nd	2.2	48.4	29.0	24.8	4.4
Inorganic/volatile acids as % of all acids	51.1	3.3	40.7	69.7	48.8	44.4	17.5
KOH titration ^b	109.4	nd	87.9	102.2	105.1	85.5	104.0

^a This portion of Sample 3 was analysed 21 days after the first portion.

^b Value expressed as a % of total acidity as measured by GC and IC.

'nd' indicates that the anion was not detected in the sample.

TABLE 4. ANIONS DETERMINED IN THE LATEX SAMPLES^a
— CONTINUOUS COLD EXTRACTION

Acid	Sample						Total
	7/1	7/2	7/3	7/4	7/5	7/6	
Myristic	0.11	0.03	0.01	nd	nd	0.02	0.17
Palmitic	1.71	0.55	0.20	0.09	0.09	0.35	2.99
Palmitoleic	0.56	0.15	0.04	0.02	0.02	0.07	0.86
Stearic	1.85	0.77	0.35	nd	nd	nd	2.96
Oleic	1.47	0.49	0.23	0.28	0.29	0.89	3.66
Linoleic	3.68	1.16	0.36	0.12	0.13	0.59	6.04
Linolenic	0.35	0.08	0.02	nd	nd	nd	0.45
Furanoic	4.72	2.60	2.32	1.52	0.93	1.48	13.58
Long-chain acids (m-equiv./kg)	14.44	5.84	3.53	2.04	1.47	3.40	30.71
Hydrochloric	0.20	0.12	0.11	nd	0.10	0.36	0.89
Glycero-1-phosphoric	0.07	0.01	0.01	nd	0.07	0.11	0.26
Phosphoric	0.01	0.01	0.02	nd	nd	0.07	0.12
Succinic	0.11	0.75	0.19	0.03	0.04	3.15	4.27
Malic	0.16	0.10	0.08	0.29	0.11	1.25	1.99
Sulphuric	0.06	0.01	0.01	nd	0.02	0.02	0.12
Oxalic	0.08	0.01	0.01	nd	0.02	0.06	0.18
Citric	0.01	nd	0.01	nd	0.01	0.08	0.10
Lactic	0.29	0.12	0.10	0.10	0.15	0.60	1.37
Formic	0.46	0.05	0.04	0.04	0.06	0.14	0.78
Acetic	1.33	0.29	0.10	0.05	0.08	0.14	2.00
Propionic	0.88	0.50	0.27	0.26	0.85	12.39	15.15
Inorganic/volatile ^b acids (m-equiv./kg)	4.19	2.89	1.30	1.10	1.77	23.25	34.50

^a Expressed as millimoles of acid per kilogramme of dry rubber from which the acids were extracted.

^b The total acid strength for the inorganic and volatile acids has been calculated allowing for the varying basicities of the different acids.

'nd' indicates that the anion was not detected in that sample.

TABLE 5. ANIONS MEASURED IN EACH SAMPLE EXPRESSED AS A PERCENTAGE OF THE TOTAL ACIDS DETERMINED BY GAS AND ION CHROMATOGRAPHY — CONTINUOUS COLD EXTRACTION

Acid	Sample						Total
	7/1	7/2	7/3	7/4	7/5	7/6	
Myristic	0.6	0.3	0.2	nd	nd	0.1	0.3
Palmitic	9.2	6.3	4.1	2.9	2.7	1.3	4.6
Palmitoleic	3.0	1.7	0.7	0.7	0.7	0.3	1.3
Stearic	9.9	8.8	7.2	nd	nd	nd	4.5
Oleic	7.9	5.7	4.8	8.9	9.1	3.3	5.6
Linoleic	19.7	13.4	7.4	3.7	4.2	2.2	9.3
Linolenic	1.9	0.9	0.5	nd	nd	nd	0.7
Furanoic	25.3	29.8	48.1	48.6	28.8	5.6	20.8
Total long-chain acids as % of all acids	77.5	66.9	73.0	64.9	45.4	12.8	47.1
Hydrochloric	1.1	1.4	2.3	nd	3.0	1.4	1.4
Glycero-1-phosphoric	0.7	0.2	0.4	nd	4.1	0.8	0.4
Phosphoric	0.2	0.4	1.0	nd	nd	0.8	0.2
Succinic	1.1	17.2	7.9	2.2	2.6	23.6	6.6
Malic	1.8	2.2	3.2	18.5	6.6	9.4	3.0
Sulphuric	0.7	0.2	0.6	nd	1.0	0.1	0.2
Oxalic	0.8	0.3	0.4	nd	1.2	0.5	0.3
Citric	0.1	nd	0.4	nd	0.6	0.8	0.2
Lactic	1.6	1.4	2.2	3.1	4.7	2.3	2.1
Formic	2.5	0.5	0.9	1.3	1.8	0.5	1.2
Acetic	7.1	3.4	2.0	1.6	2.6	0.5	3.1
Propionic	4.7	5.7	5.7	8.4	26.1	46.5	23.2
Inorganic/volatile acids as % of all acids	22.5	33.1	27.0	35.1	54.6	87.2	52.9

'nd' indicates that the anion was not detected in that sample.

Ion Chromatography Determination of Low Molecular Weight Anions

Ion chromatography was carried out on that portion of the sample which had been titrated.

These solutions contained 80% propan-2-ol which gives problems on injection due to its high viscosity. All samples were therefore diluted with four volumes of water before injection.

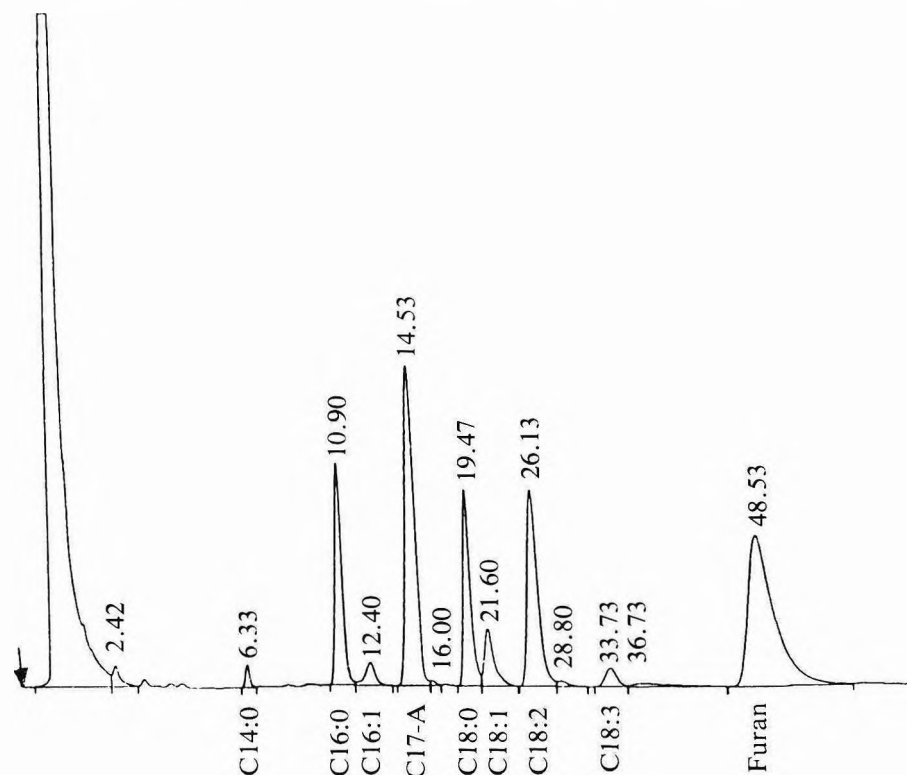


Figure 1. Chromatogram showing separation of methyl esters of fatty acids from natural rubber latex by gas chromatography.

Two different operating modes were used to separate fully all the anions present in the extract. Normal ion-exchange with HPIC-AG4 and HPIC-AS4 columns in series was used to separate inorganic anions and organic dicarboxylic anions. The eluent used was 1.5 mM sodium carbonate / 1.0 mM potassium bicarbonate / 4.0% acetonitrile. An AFS-1 suppressor fibre, immersed in 12.5 mM sulphuric acid regenerant, was used to suppress the eluent.

Ion-exclusion chromatography (ICE) was used to separate the monocarboxylic anions. The column used was an HPICE-AS1 and the eluent was 2.5 mM hydrochloric acid / 3.5% acetonitrile. A silver-loaded (HSC) ion-exchange column was used to suppress the eluent. Conductivity detection was used throughout. The IC method was the same as

that used previously to determine organic and inorganic anions in latex serum⁸.

The anions were quantified by comparison with accurately weighed standards. Typical traces are shown in Figures 2 and 3. Figure 2 shows a normal ion-exchange separation and Figure 3 an ICE separation.

DISCUSSION

It is worth noting that the total numbers of equivalents of all anions measured by GC and IC, expressed as a percentage of the total acidity measured by titration, do not vary very much even though the proportions of the total acidity measured by each technique individually vary by a large factor.

The anions measured by IC vary in an almost haphazard way, with no one anion consistently

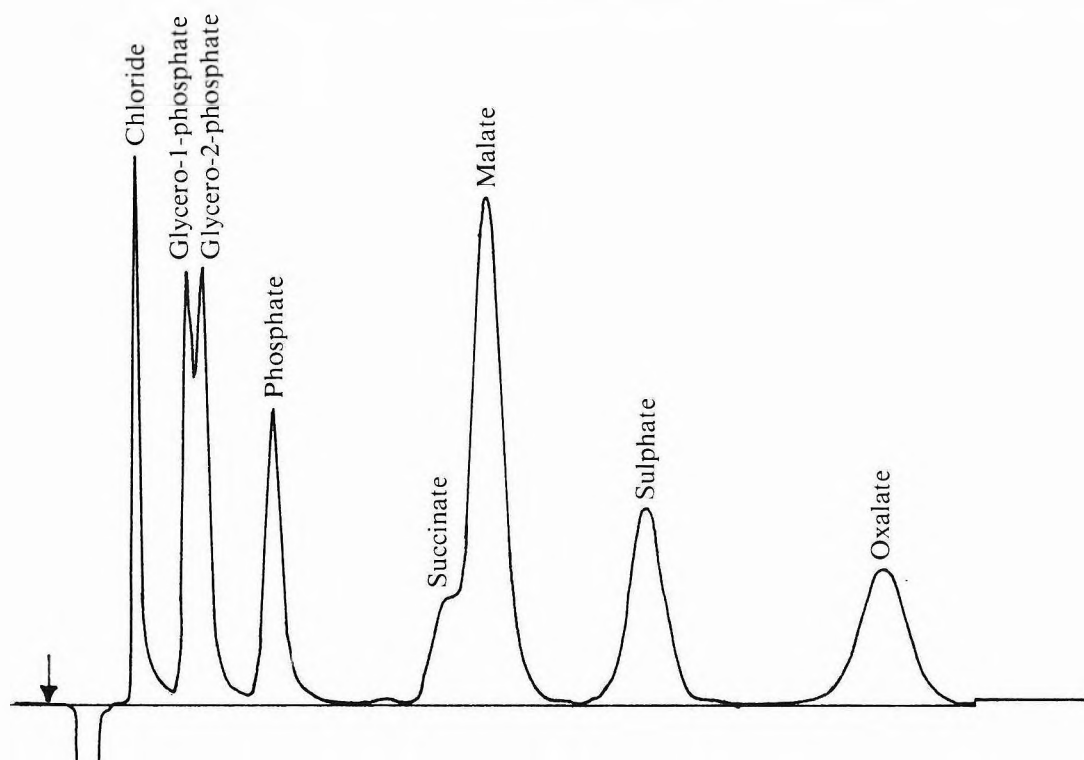


Figure 2. Chromatogram showing separation of inorganic anions and organic dicarboxylic anions from natural rubber latex using conventional ion exchange chromatography.

present or even present in the highest amount. The total measured anion levels follow the total titrated levels, but the highest is about double the lowest. The long-chain acids determined by GC are much less variable. Furanic acid is present at a relatively high level in most of the samples, and often at a higher concentration than linoleic (as shown in *Table 2* and the 'Total' column of *Table 4*) but linoleic is the long-chain fatty acid consistently present at the highest concentration, followed by stearic, oleic and palmitic acids which occur at similar concentrations.

The acids determined in the two separate extractions of *Sample 3* are similar with the main differences being a reduction in the levels of furanic acid and formic acid and an increase in propionic acid. This indicates that the fatty acids do not change significantly in relative abundance in dried latex films over a period of three weeks.

The cold extraction procedure does, eventually, extract the same amount of anions as found by titration (*Table 5*) which suggests that the anions, and especially the long-chain fatty acids measured, are really free fatty acids. The gradual increase in formic, acetic and propionic acids would normally be ascribed to increasing microbial degradation of the rubber. However, this piece of rubber was either immersed in, or saturated with, propan-2-ol throughout the extraction period and this would be expected to have been sufficient to prevent degradation. This could thus benefit from further investigation.

The titration values would not be expected to coincide precisely with the results from GC and IC as not all the acids which could contribute to the acidity as measured by titration have been determined in this study. There are several sets of anions which are sufficiently acidic to be titrated by strong alkali

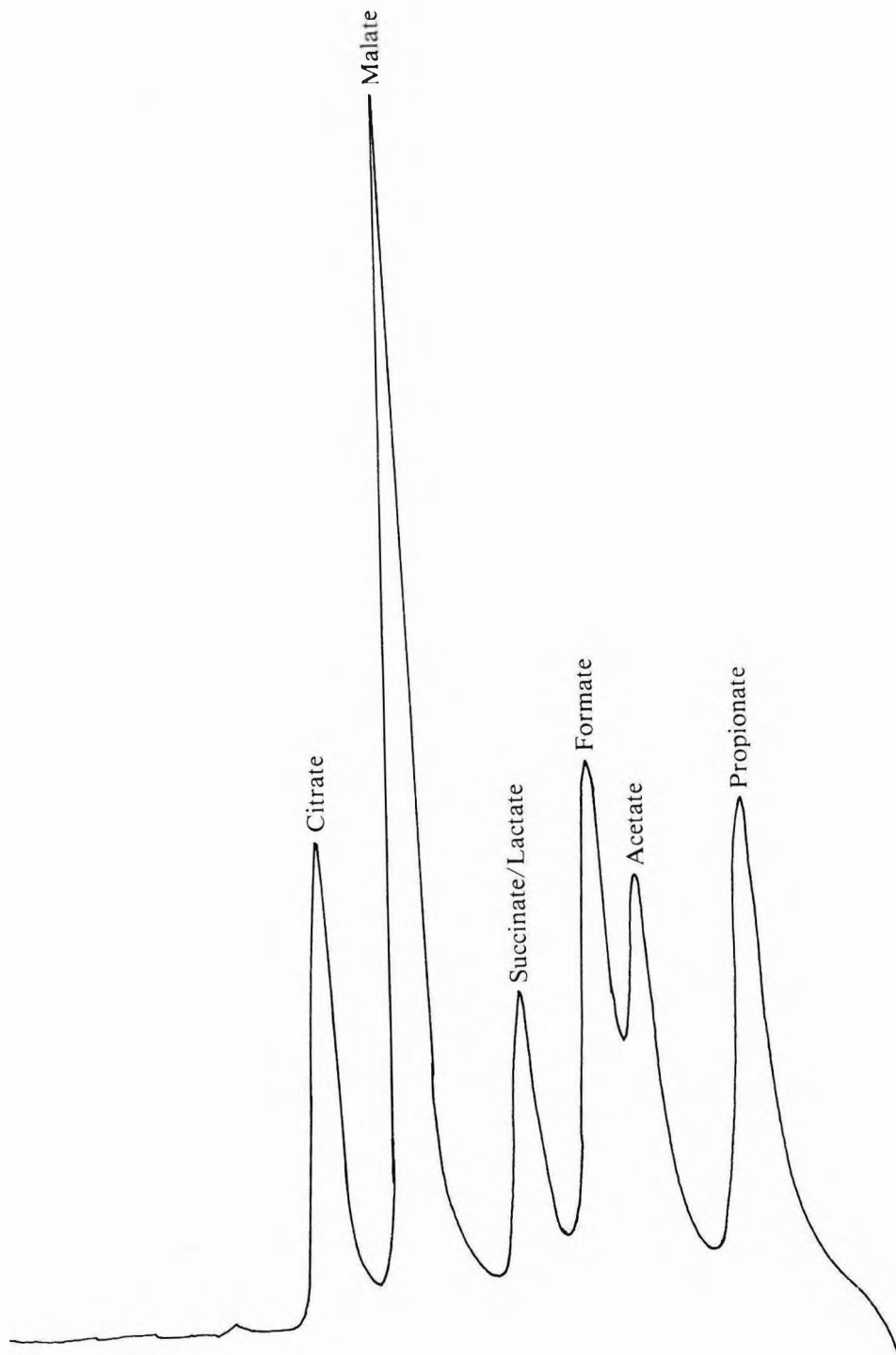


Figure 3. Chromatogram showing separation of organic anions from natural rubber latex using ion exclusion chromatography.

at pH 9-10 but which have $pK_a > 7$ and, therefore, are not acidic enough to register on the conductivity detector of the IC. Two major categories are phenolic acids and amino acids. Equally, in the titration procedure, it is possible to under-estimate the amount of acid present. Any cations, such as sodium or potassium, extracted from the rubber, will neutralise equivalent amounts of anions. This will reduce the measured titration value, but all the anions will still be measured by IC or GC. However, the good correspondence between the total anions measured by GC and IC, and the titration values, indicate that these two sources of error are either relatively small or approximately equivalent.

CONCLUSION

The results shown in *Tables 2-5* demonstrate that the common practice of converting FFA titration values to milligrammes of stearic acid will give rise to variable errors, the extent of the error depending on the actual contribution due to low molecular weight organic and inorganic anions.

There is considerable variation in the extractable acid composition, even when the source is one clone. While one would expect this to be reduced during the processing to bulk raw rubber, it is possible that important diagnostic data is being masked when only the FFA value is determined.

The combination of GC and IC is, however, capable of detecting anions equivalent to at least 85% of the FFA value for all the samples.

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Factors Affecting the NMR Technique for Estimation of Crosslink Density in Rubber Blends

P.S. BROWN* AND A.J. TINKER*

The effects of cure system, polymer molecular weight and restriction of swelling on the NMR spectra of swollen rubber vulcanisates have been investigated using a recently published technique¹. Within a single polymer type, cis-polyisoprene or cis-polybutadiene, the accelerated-sulphur cure systems produce vulcanisates having the same relationship between the volume fraction of rubber in the equilibrium swollen state (V_r) and a measure of line width, $H\%$ ¹. Swelling to less than equilibrium uptake results in a higher $H\%$, but the increase is a relatively weak function of degree of swelling and this permits confident use of the technique in the analysis of crosslink distribution in polymer blends.

For most practical purposes, rubber goods are manufactured from blends of two or more dissimilar polymers. In such blends, the physical properties are determined not only by the properties of the individual component rubbers, but also by the physical structure of the blend. To fully understand the behaviour of the blend, this physical structure must be known. Suitable techniques to determine the blend morphology and filler distribution² and the degree of interfacial bonding³ are well established. Recent papers^{1,4} report the first method for directly determining the distribution of crosslinks between the phases of a blend.

This new technique correlates the line widths observed in a continuous-wave ¹H-NMR spectrum of a blend vulcanisate to the V_r of each phase in chloroform, or to the curative concentration in the individual phases of the blend, by comparison with data from single polymer vulcanisates of the blend components. For practical convenience, the measure of line width is a ratio of signal intensities ($H\%$)¹, and $H\%$ is observed to increase smoothly with V_r in single polymer vulcanisates. It is believed that the observed line broadening is a consequence of the reduction of mobility of the polymer chain segments effected by the crosslinking network. This results in the

incomplete averaging of the magnetic fields of neighbouring atoms, both in the same chain and on adjacent chains, producing local magnetic field inhomogeneities within the sample. The consequent chemical shift anisotropies are responsible for the observed peak broadening; increased crosslinking leads *via* further restriction of chain mobility to increased $H\%$ values. Recent work using ¹³C-NMR spectroscopy to investigate swollen poly (sodium acrylate) gels supports this view^{5,6}.

For the technique to be useful in the field of polymer blend analysis, the factors affecting $H\%$ need to be understood. Various factors may influence $H\%$ through their effect on chain segment mobility. Accelerated-sulphur cure systems are known to produce chemical modification of the polymer backbone; these modifications include *cis-trans* isomerisation, the formation of conjugated polyenes and cyclic sulphides, and the addition of pendent groups to the chain⁷. Such modifications may well alter the chain segment mobility. It is possible that the potential equilibrium swelling of the phases of a blend differ due to differences in crosslink density and/or polymer-solvent interaction parameter. The V_r of the individual phases attained at equilibrium swelling of the blend may then differ from the

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

V_r that single polymer vulcanisates of similar crosslink density would attain, and this may affect the value of $H\%$.

Many rubbers degrade during mixing⁸ and the reduction in molecular weight will decrease the concentration of physically effective crosslinks by reducing the entanglement contribution to the network. Thus V_r will be reduced, but the effect on $H\%$ is less certain:

This paper aims to investigate the effect of these factors on the NMR spectra obtained from swollen rubber vulcanisates, and thereby explore the applicability of CW-¹H NMR spectroscopy to the study of vulcanised rubber blends. To simplify the analyses of the data, only single polymer vulcanisates were used in this study, but the results are applicable to blend systems.

EXPERIMENTAL

The rubbers used in this study were SMR L, SMR CV, SMR 10, *cis*-1,4 polyisoprene (SKI 3 high *cis*-1,4 polyisoprene, Tyre Research Institute, Moscow) and *cis*-1,4 polybutadiene (BR) (Europrene *cis*, 94% *cis*-1,4 polybutadiene, Enichem). Rubber chemicals were standard commercial-grade materials, solvents of AR grade except for the NMR solvents which were of spectroscopic grade [deuterium oxide (99.996 %D), deuteriochloroform and hexamethyldisiloxane (HMDS) Aldrich Chemical Company], and diisopropylazodicarboxylate (DIAD) which was used as supplied by Aldrich (97%). Cyclohexylammonium benzothiazole-2-thiolate (CBM) was prepared according to the published method⁹.

Chemical Modification of SMR L

Peroxide-cured vulcanisate: 1.4 g of a peroxide-cured SMR L vulcanisate was allowed to swell to equilibrium in toluene in the dark at 4°C. The toluene was replaced with a cold solution of DIAD in toluene (6 g/litre, the solution strength being chosen to produce a DIAD concentration of 3 g in 100 g rubber; ~1 mol%), and the sample stored for 2 h at 4°C. The sample was removed from the solution

and the solvent removed in a current of air for 2 h. It was stored *in vacuo* for 72 h, during which time the azo-ene reaction of DIAD and the rubber olefin group occurred^{1,2}, before being extracted with methanol using a cold Soxhlet apparatus, and then dried *in vacuo* to constant weight. Infra-red analysis indicated the presence of some main-chain modification, as evinced by carbonyl absorption characteristic of the 'ene' adduct, but at a level too low to quantify (< 1 mol%). A second specimen was similarly treated, omitting the DIAD from the second toluene fraction, to serve as a control vulcanisate.

Solution: 110 g of lightly milled SMR L was cut into small pieces and added to a cold solution of DIAD in toluene (3.5 g in 500 ml, 3.2 g/100 g rubber). The solution was kept at 4°C while the rubber absorbed the solvent. The resulting gel was then left in the dark at room temperature for 48 h to complete the modification reaction. The rubber was recovered by adding 1500 ml toluene and then precipitating with methanol. The swollen mass was washed several times with methanol before being dried *in vacuo* to constant weight. Infra-red analysis confirmed the presence of the modification but at a level below 1 mol%. This material was then compounded with 1.2 p.p.h.r. dicumyl peroxide and vulcanised in the usual way.

Compounding (Tables 1 and 2) was performed using a BR-size Banbury mixer and/or a two-roll mill, the curatives being added on a two-roll mill.

Samples for NMR analysis were extracted for 4 h with methanol in a hot Soxhlet apparatus and dried to constant weight *in vacuo* in the dark until required. Small slivers (~ 15 × 0.5 × 1 mm) were allowed to swell in CDCl₃ in an NMR tube to equilibrium uptake for between 36 h and 60 h in the dark. If necessary, these samples were then trimmed so as to spin freely in the NMR tube. A small amount of fresh CDCl₃ containing CHCl₃ as an internal marker and HMDS as an internal lock was added just prior to acquisition of the spectrum.

TABLE 1. FORMULATIONS OF *CIS*-POLYISOPRENE VULCANISATES

Entry	Type ^a	System	Ratio (w/w)	Sulphur (p.p.h.r.) ^b	Cure	
					Temp (°C)	Time (min)
1	CON	S-CBM	1:16	1.0	70	420
2	CON	S-MBS	5:1	1.5-2.5	140	d
3	CON	S-TMTM	5:2	1.5	150	d
4	SEV	S-MBS	1:1	0.25-2.0	150	d
5	SEV	S-CBS	1:1	1.0	150	d
6	EV	S-MBS	1:15	0.2, 0.4	150	d
7	Novor ¹¹	Novor 924 ^c -ZDMC	10:3	3.35, 6.7	160	d
8	Peroxide	Dicumyl peroxide	-	1-1.8	150	120

Entries 1-6 based on zinc oxide, 5 p.p.h.r.; Stearic acid, 2 p.p.h.r. and Flectol-H, 2 p.p.h.r.

Entry 7 based on zinc oxide, 5 p.p.h.r.; Stearic acid, 1 p.p.h.r.; Flectol-H, 2 p.p.h.r. and Caloxol W5G, 3 p.p.h.r.

^a CON: conventional, high sulphur; low accelerator ratio

EV: efficient, low sulphur: high accelerator ratio

SEV: semi-EV, intermediate sulphur: accelerator ratio

^b Concentration of Novor 924 in Entry 7 or dicumyl peroxide in Entry 8

^c Supplied by Rubber Consultants, Brickendonbury, Hertford, SG13 8NL, UK

^d Cured to the maximum torque on a Gottfert Elastograph

TABLE 2. FORMULATIONS OF *CIS*-BR VULCANISATES

Entry	Type ^a	System	Ratio (w/w)	Sulphur (p.p.h.r.) ^b	Cure	
					Temp (°C)	Time (min)
1	SEV	S-MBS	1:1	0.4-2.3	150	b
2	Peroxide	Dicumyl peroxide		0.3, 0.6	150	120

Entry 1 formulated as per Entries 1-6 in *Table 1*

SEV: semi-EV, intermediate sulphur: accelerator ratio

^a Concentration of dicumyl peroxide in Entry 2

^b Cure time as per *Table 1*

The equilibrium swelling of each vulcanisate in chloroform was determined for specimens swollen at 23°C in the dark. The swollen vulcanisate was dried *in vacuo* and the volume fraction of rubber in the swollen gel, V_r , was calculated with due allowance for the zinc oxide in the vulcanisate¹⁰.

The NMR spectra were obtained using a Perkin-Elmer R32 90 MHz continuous-wave spectrometer, interfaced to a BBC micro-computer for computer accumulation of the transients to improve the signal to noise ratio. The spectrometer was run at an 80 s sweep of 10 p.p.m. width with between forty and eighty

transients combined for each spectrum. $H\%$ was evaluated as described previously¹ using reference positions -0.2 p.p.m. and $+0.2$ p.p.m. from the olefin peak positions of natural rubber (NR) and BR respectively (Figure 1).

Sub-equilibrium swelling experiments were performed by allowing a rubber sample ($0.5 \times 15 \times 15$ mm) to swell in insufficient $CDCl_3$ to allow equilibrium uptake to be reached. A small sliver was cut from the piece and immediately placed in an NMR tube containing D_{20} and a small amount of the sodium salt²⁰ of 2,2,3,3-tetradeutero-3-trimethylsilylpropionic acid as the internal lock. The remaining swollen sample was accurately weighed and then dried *in vacuo* to allow the degree of swelling, Vr' , to be determined. The 1H -NMR spectrum of the sub-equilibrium swollen sample suspended in D_{20} was recorded as above, but combining only twelve transients to minimise solvent loss during the experiment. The olefin peak was observed to move upfield as the Vr' of the sample increased, presumably as a consequence of the changing ratio of the solvents D_{20} and $CDCl_3$ in the NMR tube. Account was taken of the movement of the peak when measuring $H\%$, the reference offset used to determine $H\%$ was 0.2 p.p.m.

RESULTS AND DISCUSSION

The possible effect of type of cure system, within the family of accelerated-sulphur systems, on the correlation between $H\%$ and Vr for polyisoprene vulcanisates is considered in Figure 2. The accelerators used include various sulphenamides and a thiuram monosulphide, and a range of accelerator: sulphur ratios was used to produce different network structures⁷ (Table 1). The CBM system is known to produce fully polysulphidic networks, typical of a conventional sulphur vulcanisate, but with accelerator-terminated pendent groups as the only type of main-chain modification⁹. The $H\%$ - Vr data for all of these vulcanisates are found to lie on a smooth curve, as did those for vulcanisates produced using a urethane (Novor) cure system¹¹. This important observation is crucial to the successful application of the NMR technique to blend

vulcanisates, because the vulcanisation chemistry operating in the individual phases is likely to be different both from each other and from that expected in the single polymers. The $H\%$ - Vr correlation is independent of the grade of NR used; indeed synthetic high *cis*-1,4 polyisoprene (SKI 3) obeys this same relationship (Figure 2).

When a peroxide-cure system is used, the resulting vulcanisates have $H\%$ values significantly lower than their accelerated-sulphur analogues (Figure 3). This difference is not observed in *cis*-BR, for which the semi-EV S/MBS vulcanisates and the dicumyl peroxide vulcanisates share the same $H\%$ - Vr correlation (Figure 4). This different behaviour of the two polymers may be associated with the methyl group of the polyisoprenes; it cannot be due to non-hydrocarbon materials in the natural rubber since SKI-3, a synthetic high *cis*-1,4 polyisoprene, displays the same response to type of cure system as NR (Figures 2 and 3).

A possible cause of the lower $H\%$ values of peroxide-cured NR vulcanisates relative to sulphur-cured vulcanisates of comparable crosslink density is the presence of backbone modifications in the latter vulcanisate type. The only polymer modification expected in the CBM vulcanisate is the addition of pendent groups to the backbone chains⁹, and the CBM vulcanisate obeys the $H\%$ - Vr correlation of the other accelerated-sulphur-cured vulcanisates. Pendent groups would seem to be the functionality introduced during accelerated-sulphur vulcanisation responsible for the greater $H\%$ values than were observed for peroxide vulcanisates.

This hypothesis was tested by introducing pendent groups onto the main chains of a peroxide-cured vulcanisate of SMR L using the well established 'ene' reaction of an azodicarboxylate with the olefin group on the polyisoprene chain¹². The modification was also performed on uncured SMR L rubber which was subsequently vulcanised using dicumyl peroxide. $H\%$ values for these pendent-modified, peroxide-cured vulcanisates

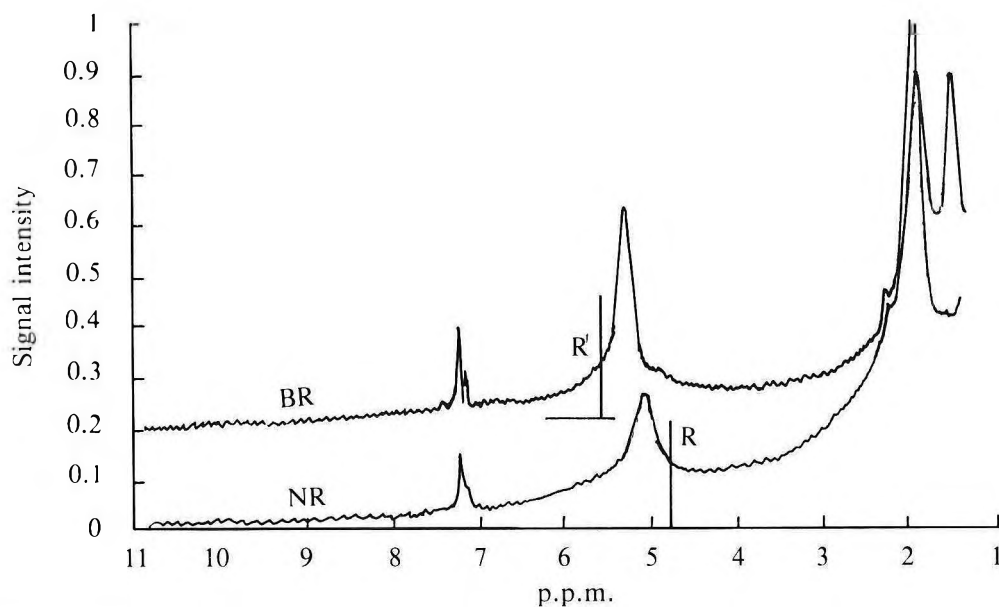


Figure 1. Continuous-wave ^1H NMR spectra of natural rubber (NR) and cis-BR (BR) swollen to equilibrium in deuterio-chloroform. The BR spectrum is displaced in intensity for clarity. The reference position used to calculate $H\%$ is shown on the side of each olefin peak (R and R' for NR and BR respectively). Both vulcanisates were cured using the semi-EV S/MBS cure system with 0.825 p.p.h.r. sulphur.

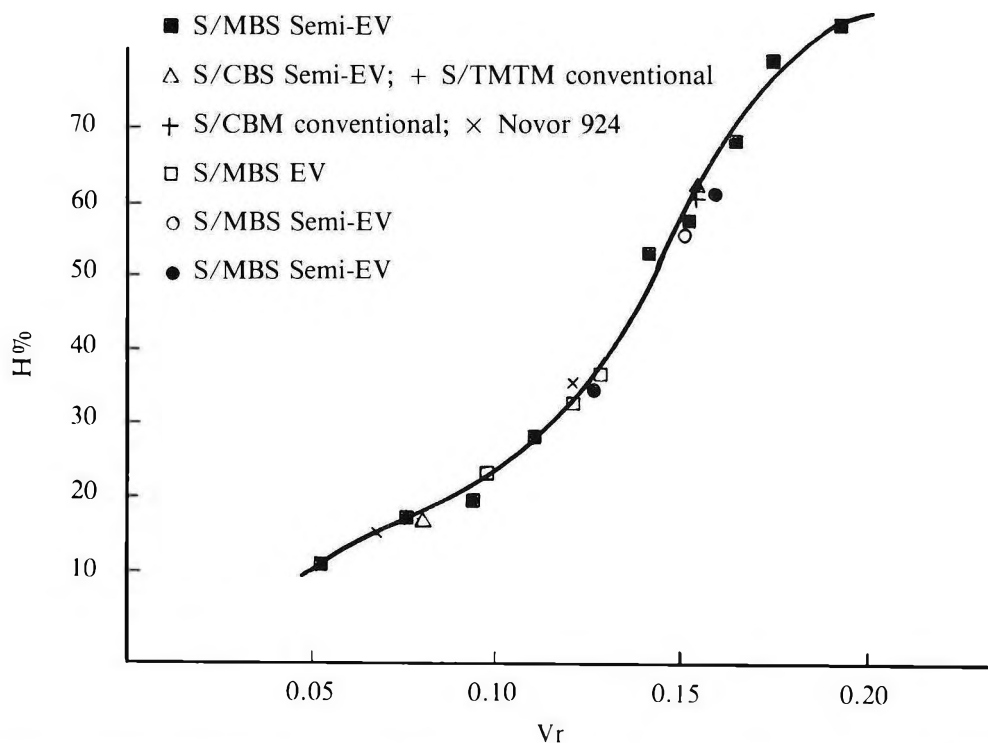


Figure 2. $H\%$ versus V_r in chloroform for accelerated sulphur cis-polyisoprene (PI) vulcanisates.

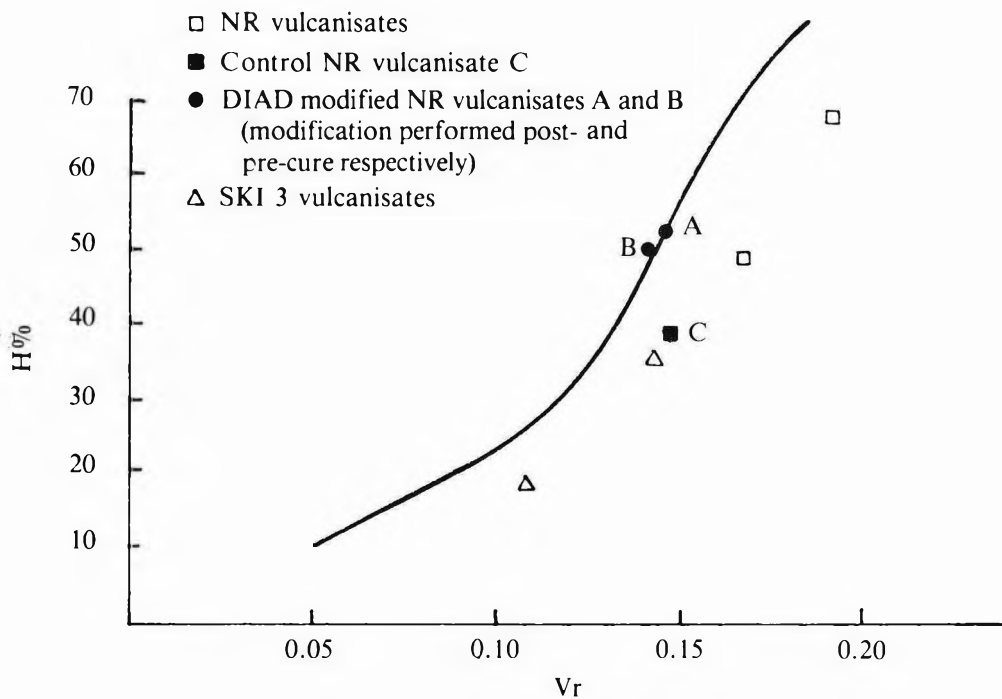


Figure 3. $H\%$ versus V_r in chloroform for peroxide-cured PI vulcanisates. The line represents the curve of Figure 2.

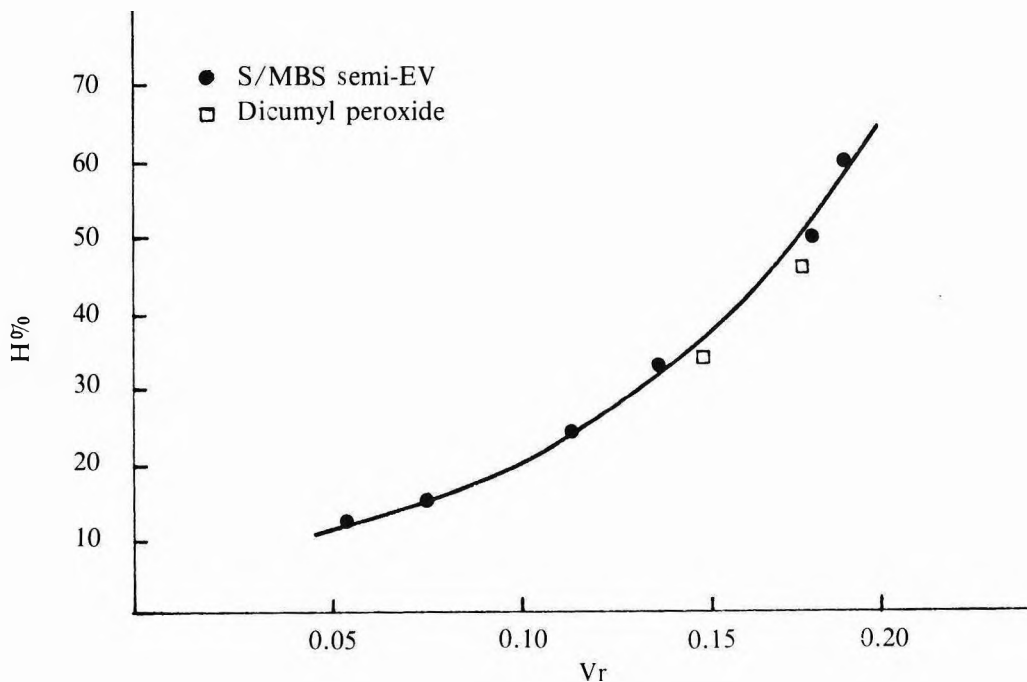


Figure 4. $H\%$ versus V_r in chloroform for BR vulcanisates.

(A and B) are higher than that of an unmodified, peroxide-cured control vulcanisate (C) of similar Vr , and are in accord with the correlation of H% and Vr of the accelerated-sulphur-cured vulcanisates (Figure 3), although this may be coincidental. It would appear, therefore, that pendent groups to the backbone chain could be responsible for the different H%- Vr relationships of these two types of NR vulcanisates. A mechanism by which the pendent groups could affect H% is a steric interaction between the pendent group and the methyl groups of the isoprene unit, acting to reduce the mobility of the chain segments in NR. Since *cis*-BR has no such group to form steric interactions with the pendants, accelerator-terminated pendent groups would not be able to exert an effect on H% for vulcanisates of this polymer in accord with observation.

To investigate the effect of the restriction of swelling of one phase of a blend by the other, samples of three of the BR vulcanisates were subjected to the sub-equilibrium technique. BR was chosen as the polymer for this particular study because of the higher intensity of the olefin peak arising, as it does, from two hydrogen atoms for every butadiene repeat unit. This produces spectra with intrinsically higher signal to noise ratios (Figure 1), allowing the number of accumulations combined in each spectrum to be kept small and thereby minimising the loss of deuteriochloroform from the swollen samples. On storage, samples showed evidence for solvent loss to the D_{20} suspension medium by the gradual appearance of a haze, presumed to be the sodium salt used to provide a lock signal or to the deuteriochloroform precipitating in the D_{20} .

H% was observed to increase with the Vr' of the sub-equilibrium swollen BR vulcanisates (D, E and F, Figure 5). The dependence of H% on the Vr' of a particular, sub-equilibrium swollen BR vulcanisate was much less than its dependence on Vr in a series of equilibrium swollen BR vulcanisates (solid line, Figure 5). Consider vulcanisate D, which has the lowest crosslink density and was compounded with 0.5 p.p.h.r. sulphur: this had an equilibrium Vr

of 0.076 and a H% value of 14. The sample of this vulcanisate swollen to the highest degree below equilibrium has a Vr' of 0.15 and a H% value of 19. To achieve this Vr value at equilibrium swelling, BR requires curatives compounded at a level of 0.9–1.0 p.p.h.r. which would give a H% value of 35. If found for a BR vulcanisate swollen to equilibrium, the observed H% value of 19 would represent a curative level of 0.60–0.65 p.p.h.r. sulphur, which is only slightly higher than that compounded. This departure of swelling from the equilibrium value ($Vr/Vr' = 0.5$) is extremely large in the context of swelling restriction, where Vr/Vr' values less than 0.8 are rare^{3,4} and is well beyond that expected in practice.

Similar comparisons may be made using the other two vulcanisates. H% therefore appears primarily to be a function of the crosslink density within the sample with a much less dependence on the degree of swelling. This observation demonstrates that for most blend combinations the NMR technique will give crosslink distribution analyses of a quantitative nature.

During compounding, certain polymers suffer reductions in molecular weight as a consequence of the work performed on the mix⁸. For such materials, it is quite likely that the molecular weight of the rubber prior to vulcanisation will vary according to mechanical history. The effect of prolonged milling of a NR mix is shown in Table 3. The breakdown was achieved by repeated passing of the mix through the tightest nip setting of a well cooled two-roll mill and represents a level of breakdown far in excess of that likely

TABLE 3. EFFECT OF MN ON H% IN NR

Mix Mn	Vulcanisate	
	H%	Vr
154 000	39.9	0.126
100 000	22.0	0.097

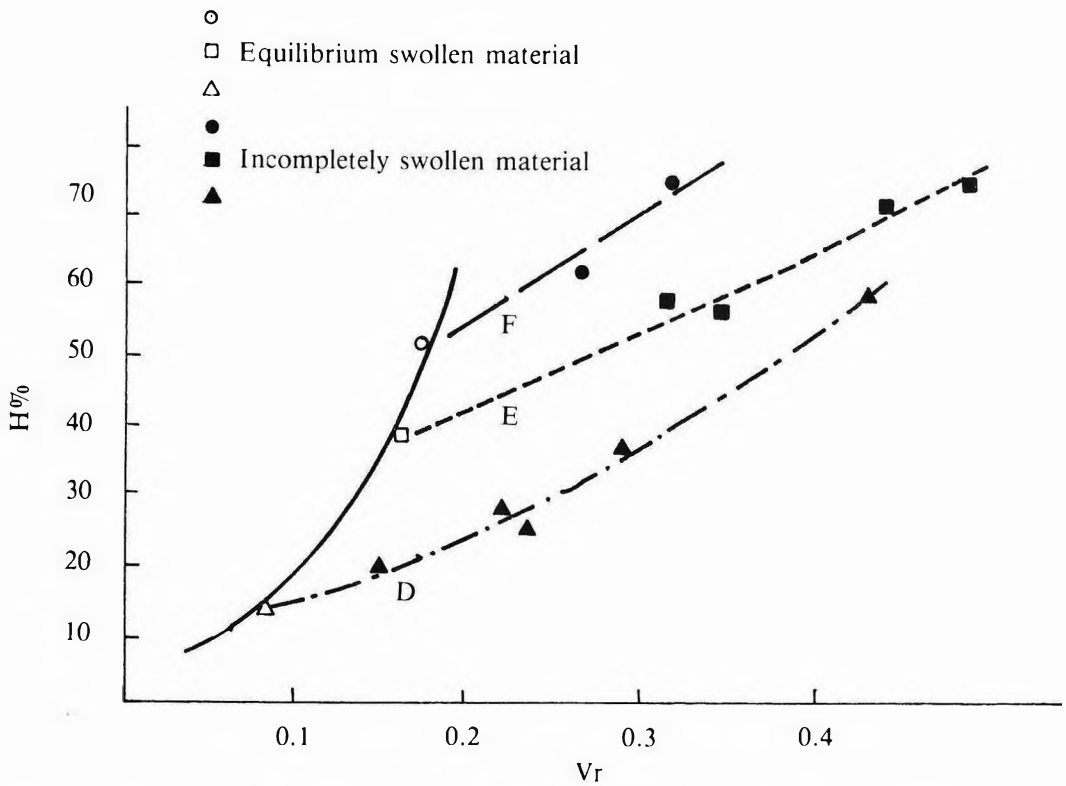


Figure 5. Sub-equilibrium swelling of BR. Solid line represents the curve of Figure 4.

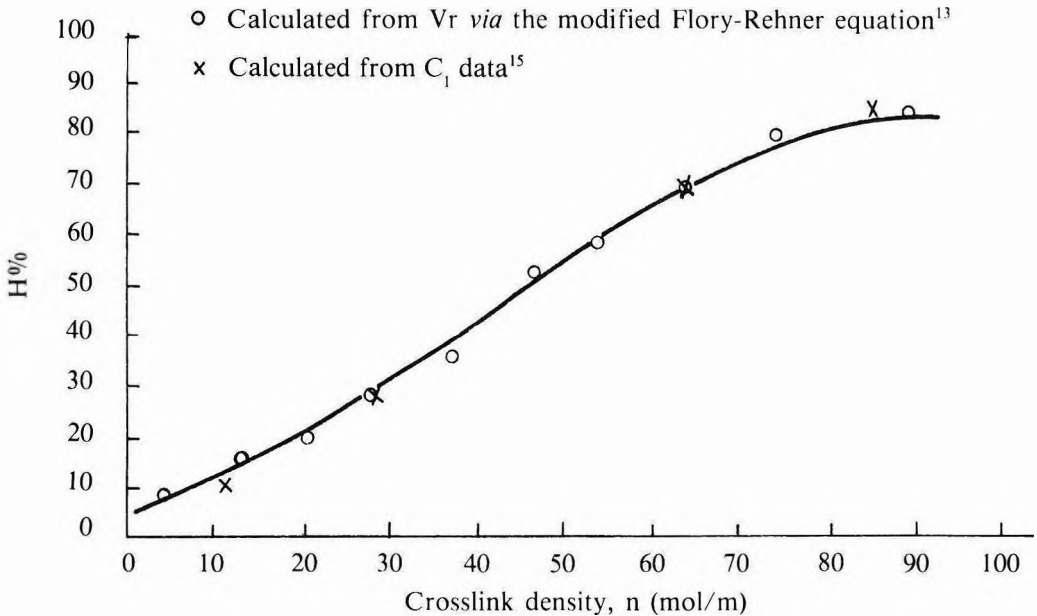


Figure 6. H% versus crosslink density (n_{phys}) for NR vulcanisates. The curve represents the best fit third-order polynomial to the data.

to be encountered during normal mixing. The vulcanisates produced from the original mix and the heavily milled mix have considerably different $H\%$ values; however, since Vr is also affected by the reduction in molecular weight, the $H\%-Vr$ relationship is maintained (*cf* Figure 2). If Vr or physical crosslink density is of primary interest, then the NMR technique gives a direct method by which these parameters may be determined. If, however, it is desired to relate the observed $H\%$ values to the effective curative levels operating within the phase, the effect of molecular weight must be allowed for in interpreting the results. In either case, the NMR technique is a valuable tool in the analysis of polymer blend vulcanisates.

CONCLUSION

Different accelerator : sulphur ratios, accelerator types and curative levels in NR, produce vulcanisates containing a range of network structures to study using NMR spectroscopy. These studies have shown that the line widths observed in the NMR spectra of equilibrium swollen vulcanisates are primarily a function of the crosslink density, including physical entanglements, within the vulcanisate. Dicumyl peroxide vulcanisates of NR have spectra with lower $H\%$ values than accelerated-sulphur vulcanisates of similar crosslink density. This difference is thought to be due to the accelerator-terminated pendent groups present in the sulphur vulcanisates, which may interact with the methyl group on the NR backbone increasing $H\%$. For *cis*-BR a different observation is made: peroxide and accelerated-sulphur vulcanisates follow the same $H\%-Vr$ correlation. In applying the NMR technique to blend analysis, one $H\%-Vr$ correlation curve for each polymer will represent the accelerated-sulphur vulcanisates. For some polymers, this correlation curve will also represent the $H\%-Vr$ relationship of peroxide-cured vulcanisates, but in other polymers, the different $H\%-Vr$ relationship requires that a separate correlation curve is produced.

$H\%$ is influenced by the degree of swelling of the vulcanisate, but this is of secondary

importance. Provided that the Vr values of the individual phases of the blend are not much greater than the equilibrium values, a condition which in almost all cases will be satisfied, the $H\%$ values obtained from the analysis of the NMR spectrum of a blend will accurately reflect the crosslink density within the phases of the blend. Thus, the application of the NMR technique of crosslink density analysis to vulcanised blends in which one phase experiences more degree of restriction of swelling, will still provide quantitative information regarding the distribution of crosslinks between the phases in the blend.

$H\%$ is a function of the molecular weight of the polymer prior to vulcanisation, having lower values at lower molecular weights; however, Vr is also a function of molecular weight, and the $H\%-Vr$ correlation is followed by NR vulcanisates produced from the same mix after different periods of mastication. Excessive mastication during the compounding of a rubber blend may thus give misleading results, particularly with respect to the level of curatives active in the phases of the blend. This is most likely to occur when the mechanical histories of the vulcanisates used to create the $H\%-Vr$, or $H\%$ -curative level correlation curves differ from that of the blend of interest. This problem can be minimised by carefully matching the compounding conditions.

The authors acknowledge that Vr is not an ideal measure of crosslink density since the polymer-solvent interaction parameter χ may well vary with degree of network modification as well as with crosslink density. Figure 6 shows how $H\%$ varies with the crosslink concentration, n_{phys} (n), in NR vulcanisates. The data is based mainly on n values calculated from volume swelling data *via* the modified Florey-Rehner equation¹³ using the χ value for NR/chloroform of Bristow and Watson¹⁴. Also included in this figure are n values calculated from C_1 data derived from stress-strain measurements¹⁵, these values being in reasonable agreement with the volume swelling derived data. There are four samples where n is obtained both *via* Vr data and *via* C_1 data. At the extremes of crosslink density, the data

do not agree as well as at the intermediate crosslink densities, but the agreement is sufficiently good to allow V_r to be used as the measure of crosslink density within this system. Further work relating H^0 to crosslink density is being carried out, and will be reported in a future publication.

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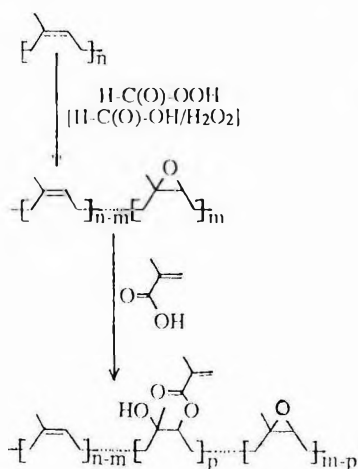
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Fixation of Methacrylic Acid onto Epoxidised Liquid Natural Rubber

D. DEROUET*, J.C. BROSSE* AND L.M.K. TILLEKERATNE**

Epoxidised liquid natural rubber (ELNR) is a derivative of natural rubber obtained by depolymerisation of natural rubber macromolecules in the latex phase using the phenylhydrazine/oxygen system followed by peracid treatment. It is a basic compound which can be subjected to chemical modifications leading to new products with various useful applications. Methacrylic acid grafted ELNR is one such product where the polymerisable unsaturated groups present on the methacrylic acid enable them to be crosslinked by UV radiation, making them useful in the enamel paint industry. This paper reports on the effects of some parameters such as the catalyst, temperature and time, on the fixation reaction between ELNR via the epoxide functions, and methacrylic acid. Addition of the acid on the epoxide functions of ELNR in the presence of p-methoxyphenol to avoid homopolymerisation of the acid can be achieved in chloroform, only in the presence of pyridine as the catalyst. Soluble photo-sensitive polymers in organic solvents are obtained.

Epoxidised liquid natural rubber (ELNR) is a derivative of natural rubber obtained by depolymerisation in the latex phase by a chemical method using the phenylhydrazine/oxygen system followed by peracid treatment^{1,2}. It is a basic compound which can be subjected to subsequent chemical modifications leading to new products with various useful applications. One such chemically modified form of ELNR is the methacrylic acid grafted ELNR:



It is well known that carboxylic acids can react on epoxide functions to form β -hydroxy esters. This reaction has been previously used to vulcanise epoxidised natural rubber (ENR) with organic acids³. The polymerisable unsaturated groups present on the methacrylic acid grafted ELNR enable them to be crosslinked by means of UV radiation, making them useful in the paint and varnish industry. UV spectroscopy has been used extensively in photo-sensitive polymers, notably by Azuma *et al.*^{4,5,6} who have studied the photo-crosslinking of rubbers containing pendant cinnamate groups.

This paper reports on the effects of some parameters such as the catalyst, temperature and time on the fixation reaction between ELNR via epoxide functions, and methacrylic acid.

EXPERIMENTAL

Methods

¹H NMR spectra were recorded on a Varian EM 90 (90 M Hz) spectrometer. Tetramethylsilane (TMS) was used as a reference and

* Laboratoire de Chimie et Physicochimie Macromoléculaire, Unité de Recherche Associée au C.N.R.S. No 509, Université du Maine, Route de Laval, BP 535, 72017 Le Mans, France

** Rubber Research Institute of Sri Lanka, Telewala Road, Ratmalana, Sri Lanka

chemical shifts are given in parts per million. IR spectra were recorded on a Fourier transform Perkin-Elmer 1750 spectrometer. Titrations were achieved on a Metrom potentiometer (Impulsomat 614; Dosigraph 625; pH meter 632 and Dosimat 655).

Materials

Solvents were purified by the usual methods. The 30% ELNR sample, supplied by the Institute of Applied Research on Polymers of Le Mans (IRAP), was purified by dissolving in toluene followed by filtration through a No. 3 sintered glass crucible under suction and precipitation in methanol. The purified sample was dried up in vacuum at 60°C, until constant weight was obtained. Analysis of the level of epoxidation of the ELNR sample was cross checked by ¹H NMR spectrometry.

Methacrylic acid (Janssen product; 98.5% of purity) was purified by distillation under reduced pressure, a few hours before use. The collected fractions from the distillation were analysed by ¹H NMR, to verify that they are free from polymerised contaminants, and stored under refrigeration until they are used.

p-Methoxyphenol used as the crosslinking inhibitor is a Aldrich product (purity = 99%). Tetramethylammonium methacrylate was prepared by neutralising a known weight of the distilled methacrylic acid with 0.45 N solution of tetramethylammonium hydroxyde in methanol (Aldrich product). The end-point was detected by potentiometric titration. The salt thus obtained at pH 11.4–11.7 was isolated after removal of the solvent and dried in vacuum at 50°C. Its purity was determined by ¹H NMR spectroscopy.

Pyridine, potassium hydroxide and triphenylphosphine were pure commercial products.

Preparation of Stock Solutions

A 3 M solution of methacrylic acid containing the catalyst (tetramethylammonium methacrylate, potassium hydroxide, triphenylphosphine or pyridine) in the molar ratio

[catalyst]/[methacrylic acid] = 0.1 was prepared in chloroform for the coupling reactions. Where tetramethylammonium methacrylate was used as the catalyst, the solution was prepared as follows: 6.46 g of methacrylic acid (7.5×10^{-2} mol) freshly distilled was mixed with 20 ml of methanol and then treated with 0.45 M tetramethylammonium hydroxide solution to the neutral point. To the dry salt obtained after evaporation of the solvent, 64.6 g of methacrylic acid was added and the solution was made up to 250 ml with chloroform.

A second 3 M solution of oxirane functions was prepared by dissolving 72.8 g of 30% epoxidised ELNR in chloroform and the solution was made up to 100 ml.

Procedure

5 ml of the ELNR solution and 5 ml of the acid stock solution containing one of the three catalysts in the molar ratio [acid]/[epoxide]/[catalyst] = 1:1:0.1 mixed with 1.5×10^{-2} mol of the inhibitor (p-methoxyphenol) were heated to 100°C in a thermo-statically controlled oil bath and 2 ml samples of the mixture were pipetted out at different intervals of time ranging from 5 h to 10 h. Those samples were tested for residual acid content by means of potentiometric titration with 0.45 N solution of tetramethylammonium hydroxyde in methanol.

When the residual acid concentration reached a steady value, the solution mixtures in the tubes were taken out, coagulated with excess of methanol and dried in vacuum at room temperature until constant weight was reached for NMR analysis.

RESULTS AND DISCUSSION

Four types of bases were used as the catalyst to couple the oxirane of ELNR with methacrylic acid:

- Tetramethylammonium methacrylate, according to Soutif Procedure⁷
- Potassium hydroxide
- Pyridine
- Triphenylphosphine.

Most of the coupling reactions carried out in this study were done with the tetramethylammonium salt of the acid as the catalyst for the reaction according to earlier workers⁷ who have shown that the best results of fixation of a carboxylic acid on an epoxide were obtained in the presence of this catalyst. According to them, all the experiments were carried out in chloroform, with the molar ratio [acid]/[epoxide]/[catalyst] = 1:1:0.1.

To avoid homopolymerisation of the acid in these experiments, p-methoxyphenol was used as the inhibitor in the mixture. It was shown that the concentration of the inhibitor in the medium played a prominent part in the reaction: in all cases where p-methoxyphenol was used in concentrations less than 1.5×10^{-2} mol under the conditions used for the reaction and in the cases where it was not used, there was a thick precipitate formation. This precipitate which, after washing and drying, was insoluble in any solvent, was identified as the polymerised or crosslinked acid. However, the crosslinking reaction was completely suppressed when 1.5×10^{-2} mol or more of the p-methoxyphenol was introduced. It was also noticed that in the presence of the tetramethylammonium salt of methacrylic acid, the tendency of the acid to homopolymerisation was much higher than with the other catalysts.

When ELNR modification was carried out with tetramethylammonium methacrylate, it was observed that there was no change in the initial acid content in the mixture even after 72 h heating at 100°C. However, when there was no inhibitor in the system, a white precipitate of homopolymerised acid formed rapidly, lowering the residual acid content. Further, the ¹H NMR spectrum of the rubbery product recovered by methanol coagulation did not show any sign of acid fixation on the ELNR or even a drop in the epoxide content in the original ELNR used. Similar results were obtained in the presence of KOH as the catalyst because it had no catalytic effect.

When triphenylphosphine was used as the catalyst in the same molar ratio as above and in the presence of the inhibitor, it was

observed that the residual acid content decreased gradually and reached a steady level at 0.083 mol in about 73 h. The level of fixation calculated on the basis of the change in acid concentration at this point is 10.8% (Figure 1). However, in the ¹H NMR spectrum of the polymer recovered by methanol coagulation, there was no sign of methacrylic acid fixation on ELNR. But the signal due to the resonance of the hydrogen atom attached to the epoxide group disappeared after heating for 62 h.

In a pyridine-catalysed system in the presence of p-methoxyphenol, it was observed that the residual acid content decreased to 0.065 mol in about 75 h and according to that, the level of fixation at this point was 13.3% (Figure 2). Further, there was clear evidence on the ¹H NMR spectrum of ELNR recovered by methanol coagulation that there was methacrylic acid fixation on the ELNR. At $\delta = 5.75$ and 6.3, there were resonance signals due to the two protons attached to the double bond. The resonance bond at $\delta = 2.7$ in the ¹H NMR spectrum of pure ELNR due to the hydrogen on the epoxide ring disappeared after the reaction. At temperatures below 100°C, there was no evidence of any grafting taking place with any of the above catalysts. Even at temperatures above 100°C, such as 110°C and 120°C, there was no improvement in the grafting efficiency while there were problems to retain the solvent chloroform in the reaction mixture which is extremely volatile at such high temperatures. Hence, all the results reported in this paper were obtained at 100°C, which was found to be the most suitable temperature for this reaction.

CONCLUSION

Synthesis of photo-sensitive polymers by grafting methacrylic acid onto ELNR can be achieved only in the presence of pyridine as the catalyst. Interesting yields of addition of the acid on the epoxide functions in chloroform medium were obtained at 100°C with the initial molar ratio [acid]/[epoxide]/[catalyst] = 1:1:0.1 after 72 h of reaction. Though the percentage of grafting achieved by this method was low, the presence of a few unsaturated

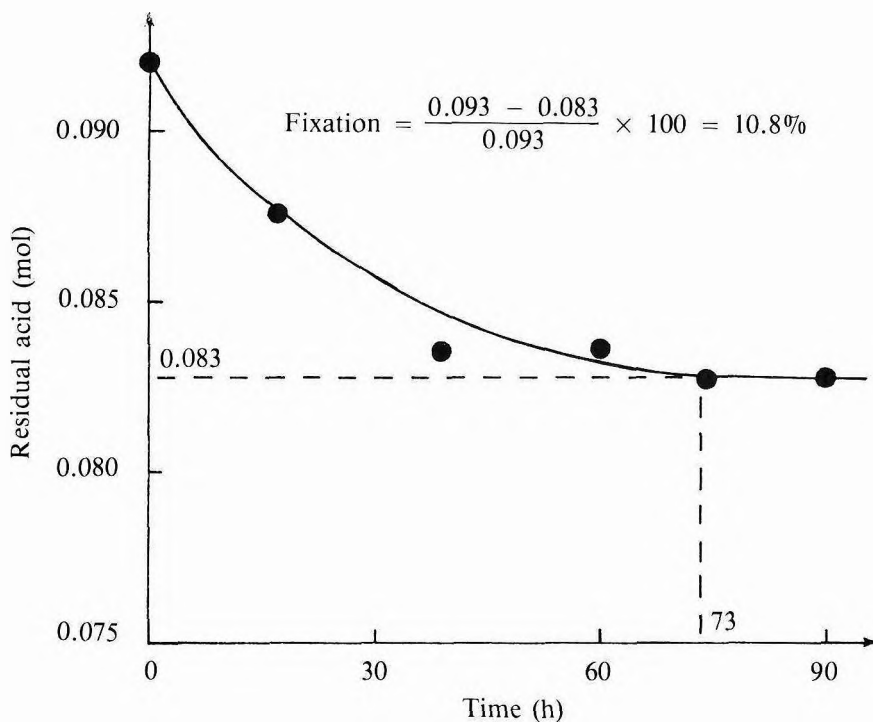


Figure 1. Change in acid molarity during the ELNR/methacrylic acid reaction catalysed by triphenylphosphine at 100°C.

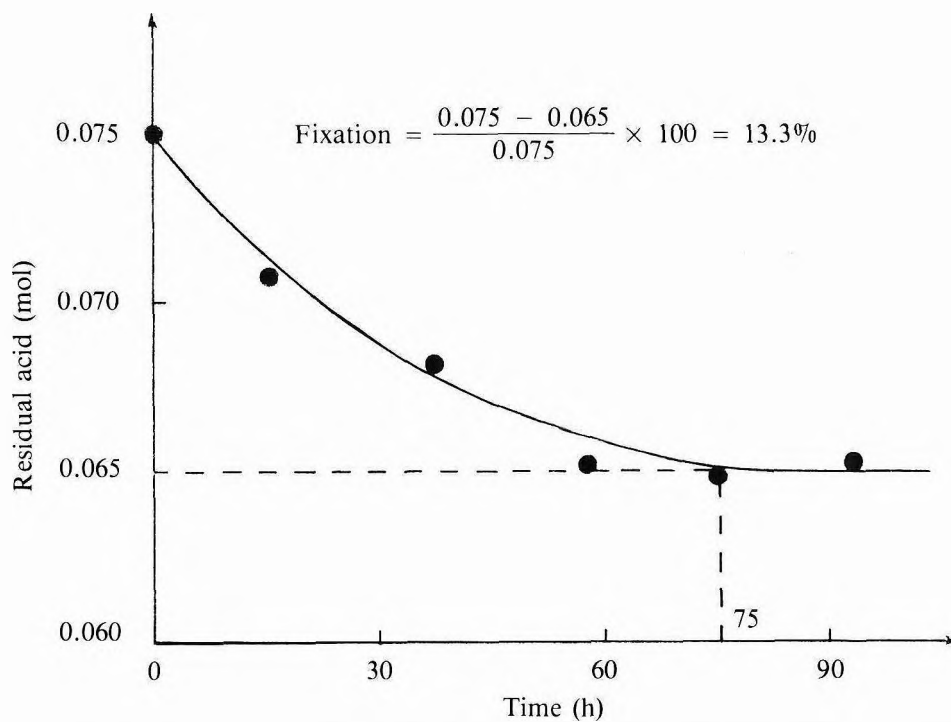


Figure 2. Change in acid molarity during the ELNR/methacrylic acid reaction catalysed by pyridine at 100°C.

groups on the grafted monomer was sufficient to enable them to be photo-crosslinkable by means of UV radiation. Hence, the product obtained is expected to be a useful industrial material in the future.

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