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THE INFLUENCE OF CURING SYSTEMS ON THE PROPERTIES OF NATURAL RUBBER

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SYNOPSIS

After a brief historical introduction the influence of curatives on the chemical structure of vulcanizates is discussed. Emphasis is given to physically important features of network structure such as crosslink density, crosslink type, and various main-chain modifications. The significance of extra-network materials such as curative residues and zinc soaps is introduced. Nonsulfur systems are briefly considered.

The effects of differences in network structure and in extra-network materials on aging properties is outlined with special emphasis on the importance of total combined sulfur, conjugated triene groups, and curative residues. The special problem of finding suitable antioxidants and antiozonants for peroxide cured rubber is mentioned. The influence of different curing systems on the crystallization of natural rubber both at low temperatures and at large extensions is described and shown to be a similar function of vulcanizate structure in both cases when compared at constant degrees of crosslinking. Problems in the interpretation of stress–strain behavior are reviewed.

Changes in the C_1 term of the Mooney–Rivlin relation can only be interpreted as changes in crosslink density or as a filler stiffening effect of insoluble extra-network material. Changes in the C_2 term of this relation also take place as the curing system is changed and are correlated with inelastic behavior. Analysis of stress–strain relations at high strain using the Martin–Roth–Stiehler equation indicates significant differences in the strain-induced crystallization behavior of vulcanizates based on various curing systems, even when compared at similar crosslink densities.

The inelastic stress–strain properties of natural rubber vulcanizates are divided into three main regions: (a) the glass transition region; (b) the chemical transition region, and (c) the intermediate region. The effects of network structure and extra-network materials in each region are considered separately. In particular, the effects of zinc soap structurization on stress relaxation behavior in the intermediate region is described, including the likely mechanisms by which rubber-soluble zinc soaps reduce the stress relaxation rate.

The influence of curing systems on the strength properties of homogeneous and isotropic natural rubber vulcanizates is described briefly, with particular emphasis on the role of polysulfidic crosslinks and main-chain modifications.

INTRODUCTION

In its origins and throughout most of its development, the rubber industry is deeply rooted in empiricism. This most profoundly applies to the technology of compounding which evolved into a highly developed art long before the chemical significance of the various additives was understood. In many respects the description of rubber behavior and its relationship to the service performance also has a long history of empiricism, which has resulted in an almost bewildering array of specification tests. Most of these are only vaguely related to service performance and often represent highly composite properties.

Although there had been isolated scientific studies on rubber behavior, including the remarkable works of Joule and that of Boltzmann on viscoelasticity, in the nineteenth century, the subject gained real impetus in the 1920's and 1930's with the evolution of the concepts of macromolecules and crosslinking.

The inauguration of the British Rubber Producers' Research Association in 1938 must be acknowledged as a major landmark in the progress of elastomer science, as evidenced by the fact that, some 35 years later, more than half the contributors in this symposium are either past or present staff of that organization. Indeed the name of the key figure honored in this symposium appeared in the first Annual Report (1938) of BRPRA as follows: "A physicist Dr. L. R. G. Treloar working under the supervision of Dr. J. K. Roberts is endeavoring to reach a better understanding of the relation between physical properties and chemical structure. Meanwhile attempts are being made to discover means for the synthesis of polymers of predetermined chemical structure." With changes only in the names and disciplines of individuals the same paragraph could well appear in a current MRPRA Annual Report.

Although the nature of the base polymer is the major factor determining properties, the curative system is almost comparably important and forms the subject of this paper.

VULCANIZATION

The most profound effect of curatives on rubber properties is, of course, the process of vulcanization. Initially this was effected by the addition of elemental sulfur to the masticated raw rubber which was then subjected to many hours of heating. Ironically, this very simple recipe has since been found to lead to a particularly complex vulcanizate structure [1]. Limitations in the physical properties of such vulcanizates, coupled with the long vulcanization times required, led to the search for improved formulations.

The typical present-day curing system is still based on sulfur as the main vulcanizing agent but contains (Table I) one or more vulcanization accelerators (generally mercaptobenzthiazoles, dithiocarbamates, or their derivatives), zinc oxide and a fatty acid to "activate" the accelerator. In addition to the actual curatives, a practical rubber compound will also generally contain antioxidants, antiozonants, stiffening fillers such as carbon black, and certain process aids.

The essential chemical feature of vulcanization is the crosslinking of the long-chain rubber molecules to form a network. This feature had long been

TABLE I

Typical Curing Systems[a] for Natural Rubber

pphr	Conv.	Semi-EV	EV	Soluble-EV	Peroxide
S	2.5	1.2	0.53	0.7	
CBS[b]	0.6	1.8			
MOR[c]			2.1	1.7	
TMTD[d]			1.0		
TBTD[e]				0.7	
DCP[f]					1.8

[a] Levels are per 100 of rubber with which will also be mixed 3-5 parts zinc oxide, 1-3 parts stearic (or other) acid, fillers, and antidegradants. Peroxide vulcanizates do not normally contain zinc oxide or additional organic acids.

[b] N-Cyclohexylbenzothiazole-2-sulfenamide.
[c] 2-(Morpholinothio)-benzothiazole.
[d] Tetramethylthiuram disulfide.
[e] Tetrabutylthiuram disulfide.
[f] Dicumyl peroxide.

suggested but was not really proven until the classic work of E. H. Farmer and his colleagues on "model" compounds [2] at BRPRA. Indeed, there were quite eminent rubber scientists who disputed the crosslinking theory of vulcanization right up to the late 1940's [3]. The various recipes now used differ mainly in the rate and kinetic form of vulcanization and are selected according to the requirements of the particular processes of fabrication being used.

The main structural features of a sulfur vulcanizate are shown in Figure 1. The main consequences of such structural differences are as follows: (1) The number distribution of sulfur atoms in the crosslinks is important in the context of reversion resistance, hysteresial properties, especially at high temperature, and in strength properties. (2) The number of cyclic sulfide structures is important in rubber crystallization phenomena and in the resistance to oxidative aging. (3) The pendant accelerator groupings ($-S_xAcc$)

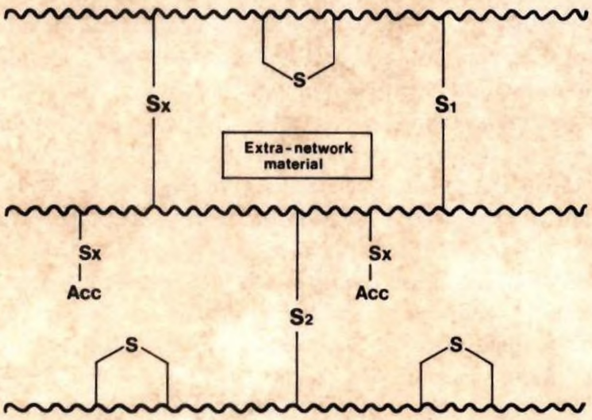

FIG. 1. Schematic diagram of structure of natural rubber vulcanized with sulfur and accelerator.

are significant as intermediates in the vulcanization process and, because of their large dipole moments, may be capable of strong association and thus act as labile crosslinks. Evidence for this is, however, very meager [4].

The extra-network material consists of a mixture of both soluble and insoluble debris from the compounding ingredients and naturally occurring "nonrubbers." The totally insoluble fraction includes the original fillers, zinc oxide, zinc sulfide (a by-product of the vulcanization process) and natural proteins. The soluble and partially soluble fraction includes the zinc salts of the accelerator and its decomposition products, zinc fatty acid soaps, amines from the decomposition of some accelerators, and, of course, it will include the antioxidants and other nonrubber constituents present in the unvulcanized compound. The extra-network material can have profound effects on the oxidative aging and long-term hysteresial properties of natural rubber, albeit for different reasons, and will be discussed later.

A number of more detailed structural features of vulcanizate networks have also been elucidated which, to some extent, clarify the mechanisms of the process [5]. However, the precise significance of such features in respect of vulcanizate properties has not to date been clearly established, although some overall differences in vulcanizate stability could be due to them [6, 7].

The most technologically significant differences in vulcanizate structure occur when the ratio of accelerators to elemental sulfur is changed [8]. When this ratio is low (0.5 CBS/2.5 S, for instance) the vulcanizate (at the so-called optimum cure) consists largely of polysulfidic crosslinks with some mono- and disulfide crosslinks as well. A significant proportion of the combined sulfur is also present as five- or six-membered cyclic monosulfide structures. A few accelerator pendant groups are also present. With increasing cure time (especially at high temperature) the number of sulfur atoms in the crosslinks is slowly reduced, and at the same time some of the crosslinks disappear (reversion). During reversion a considerable increase in the concentration of cyclic sulfides takes place, and some conjugated olefinic structures appear as a result of crosslink destruction.

With a high ratio of accelerators to elemental sulfur (6.0 CBS/0.4 S, for instance) the initially formed polysulfide attachments (including pendant groups and crosslinks) are rapidly converted to mono- and disulfidic crosslinks, with only minor amounts of crosslink destruction and cyclic sulfide and triene formation. With this system (the so called "efficient vulcanization" or EV system) the level of accelerator pendant groups is significantly higher [9].

In the absence of added accelerators ("simple" sulfur vulcanizates) the vulcanization process depends much more on the presence of a small and variable level of "natural" accelerators in natural rubber. Apart from differences in the structure of the crosslink attachment to the rubber chain, such a system also produces a high level of cyclic sulfide and triene groups along the rubber chain. The crosslinks are very polysulfidic in character [1] and strongly prone to reversion.

Running alongside the continuing development of sulfur-based curing systems has been the search for nonsulfur curing systems. The motivation for such a search has, in fact, been a double one. In the first place it was, and is, the technologists' understandable desire to produce compounds with better properties. In this respect it must be admitted that, without a deeper understanding of the principles relating properties to structure than has existed hitherto, the approach has so far been essentially, and of necessity, an ad hoc one, with little chance of "tailoring" a better overall balance of properties.

The second and more fundamental motivation has been the need to develop a stoichiometric curing system with which vulcanizates having clearly defined chemical crosslink densities could be produced. Although such a stoichiometric crosslinking system has not yet been produced for natural rubber, it has been shown that when certain organic peroxides are used as vulcanizing agents, the chemical crosslink density in natural rubber can be determined by methods which involve careful analysis of the reaction products of the peroxides [10]. The network so produced is chemically very simple, having virtually no main-chain modifications [11]. The main structural features of different vulcanizates are shown in Table II.

AGING

The slow deterioration of vulcanizates by moderate heat in the absence of oxygen is really a continuation of the vulcanization chemistry discussed in the last section, and will not be considered further here.

More conventionally, the term "aging" is used to describe the deterioration of rubber by reaction with atmospheric oxygen, although clearly both processes may take place simultaneously. The subject of aging in rubber has occupied as much of the chemists' efforts as that of vulcanization and cannot be fully covered within this one lecture. Several excellent reviews are available [12]. Comments here will be confined to the influence of curing systems.

A practical vulcanizate contains several types of antioxidant material. The compounder generally adds one or more synthetic antioxidants of the

TABLE II

Structural Features of Different Vulcanizates

Curing system	Crosslink types	Main-chain modification level	Pendant group level	Triene group level
Simple S	$-S_X-$	High	Very low	High
Accel. high-S (conv)	$-S_X-$ $-S_2-$ $-S-$	Moderate	Low	Moderate
Accel. low-S (EV)	$-S-$ $-S_2-$	Low	Moderate	Low
Peroxide	C–C	Nil(?)	Nil(?)	Low

aromatic amine or phenolic type. In addition, commercial grades of natural rubber contain a complex mixture of natural antioxidants (as well as some pro-oxidants). The reaction residues of some vulcanization accelerators (particularly thiurams and dithiocarbamates) also act as powerful antioxidants. Finally, the sulfur modifications introduced into the network profoundly change the rate and nature of the autoxidative reactions. Although in the absence of other antioxidants a number of sulfur compounds act as oxidation inhibitors, they frequently "antagonize" the action of more conventional antioxidants. In consequence, the higher the level of combined sulfur in a vulcanizate the more difficult it is to protect it against oxidation [13].

Both EV systems and peroxide systems with added antioxidant give vulcanizates which are therefore, in comparison with those given by conventional systems, particularly resistant to aging. In thiuram-based EV systems the dithiocarbamates resulting from the decomposition of the thiuram are themselves very effective antioxidants. Unfortunately, the choice of antioxidants with peroxide-curing systems is very limited, since most of them interfer with peroxide crosslinking. Antioxidants also having an antiozonant action are particularly difficult to find for peroxide vulcanizates.

During aging, both polymer chain scission and crosslinking reactions take place, the balance of which determines whether softening or hardening occurs. When the aging is advanced, a significant degree of main-chain modification by structures that contain oxygen affects other physical properties, as will be discussed later.

CRYSTALLIZATION OF NATURAL RUBBER

One of the most significant characteristics of natural rubber is its tendency to partially crystallize at low temperatures or under stress. The crystallization at low temperature is generally undesirable and this provided much of the early motivation to modify natural rubber that led to the discovery of vulcanization. By contrast, the crystallization which occurs at high strain is undoubtedly the basis of the high tensile strength of natural rubber. Although reinforcing fillers profoundly improve the strength of synthetic noncrystallizing elastomers at room temperature, the superior tensile strength of natural rubber at elevated temperatures is still clearly evident (Fig. 2). The fatigue life of natural rubber under nonrelaxing conditions is also far superior to that of synthetic rubber (Fig. 3).

The crystallization of natural rubber at low temperature is, at least by comparison with that at large strains, reasonably amenable to experimental study using X-ray methods, dilatometry, stress relaxation, electron microscopy, and microcalorimetry. The usual factors of nucleation and growth are recognized and a kinetic theory is well developed. The retarding effects of crosslinking and main-chain modifications on low-temperature crystallization in natural rubber are also theoretically well described [14].

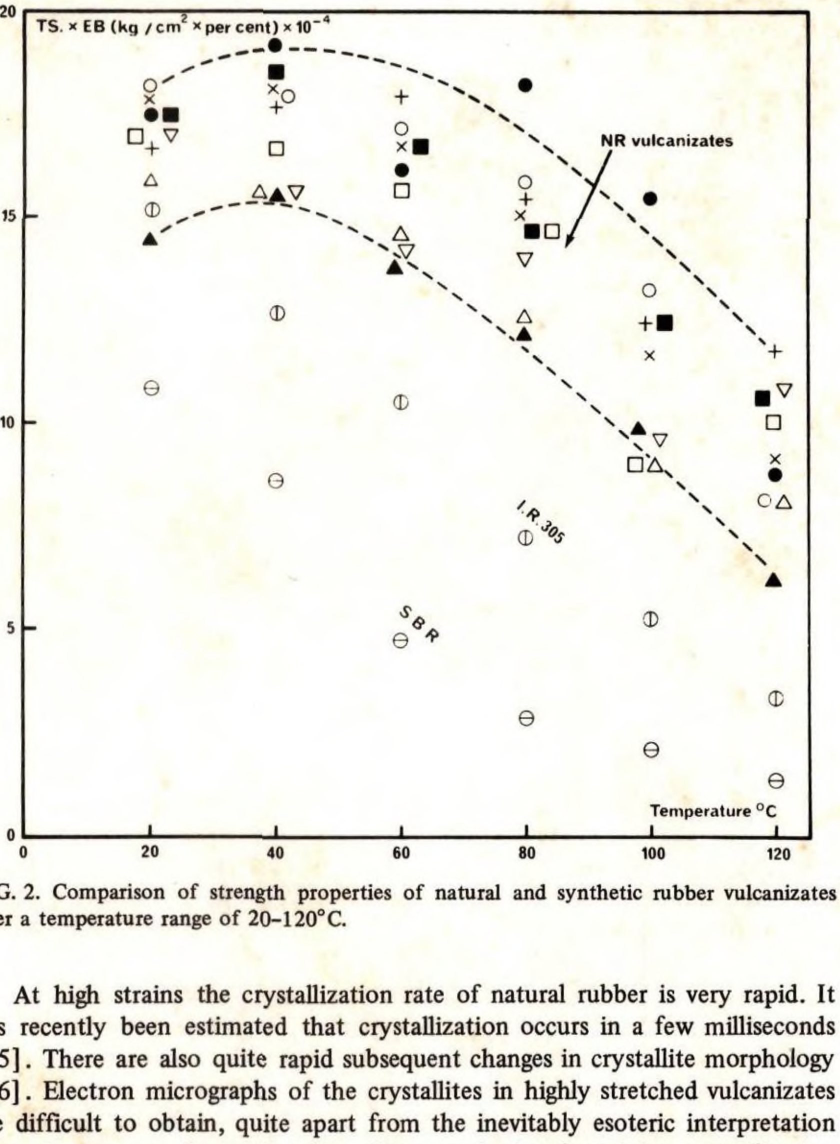

FIG. 2. Comparison of strength properties of natural and synthetic rubber vulcanizates over a temperature range of 20–120°C.

At high strains the crystallization rate of natural rubber is very rapid. It has recently been estimated that crystallization occurs in a few milliseconds [15]. There are also quite rapid subsequent changes in crystallite morphology [16]. Electron micrographs of the crystallites in highly stretched vulcanizates are difficult to obtain, quite apart from the inevitably esoteric interpretation of such pictures. Somewhat less direct methods of studying crystallization effects at high strain have therefore been used [17] and will be discussed later.

It is perhaps ironic to note that the early unaccelerated sulfur vulcanizates with their highly modified networks were extremely resistant to low-temperature crystallization. Although many properties have been greatly improved by the use of modern curing systems, the resistance to crystallization at low temperature is now comparatively poor (Fig. 4), particularly in the case of peroxide or EV systems.

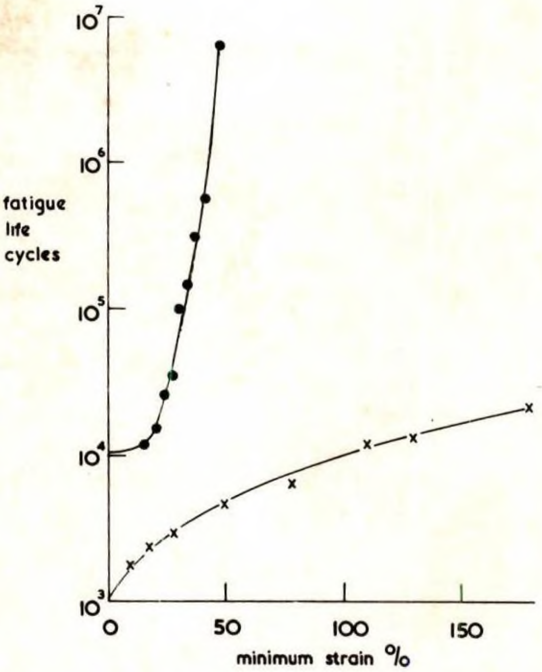

FIG. 3. Fatigue life as a function of minimum strain of cycle (maximum strain is 250%): (●), natural rubber, (x), SBR.

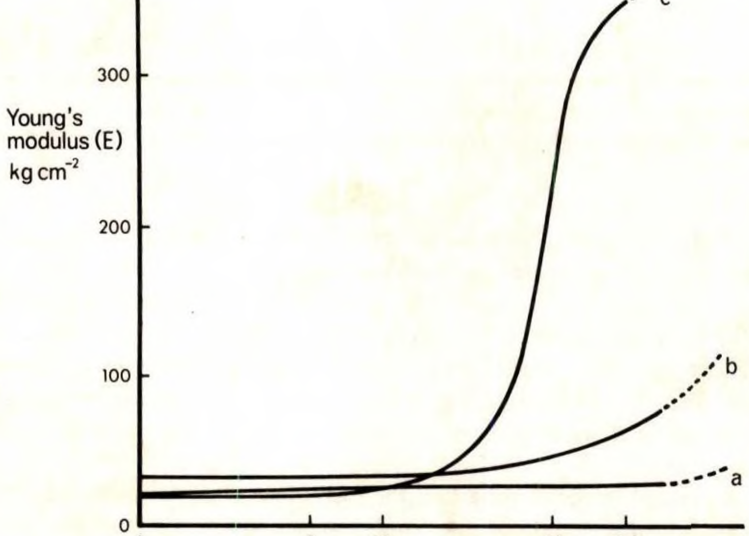

FIG. 4. Time-dependent changes in Young's modulus at −10°C for some typical bridge-bearing vulcanizates. (a) Natural rubber/conventional accelerated sulfur formulation; (b) crystallization-resistant polychloroprene formulation; (c) natural rubber/fully soluble EV formulation.

STRESS-STRAIN RELATIONSHIPS

Understanding the stress-strain relationships of rubber is not only a fundamental challenge to physics, it is also of vital importance to rubber chemistry, to rubber technology, and to the engineering design of rubber components.

Much of the chemist's knowledge about the structural features of vulcanized networks is obtained from changes in the crosslink density after treatment of the vulcanizate with various chemical reagents [18]. The direct measurement of crosslink density by chemical analysis is not yet possible for most natural rubber vulcanizates including those produced by sulfur systems. The stress-strain behavior of rubber is therefore particularly important as a means of determining crosslink density, in spite of theoretical problems of interpretation.

To the engineer concerned with the design of components the stress-strain theory of rubber is essential for the prediction of the load-deformation and failure characteristics of a component in various modes of deformation. Finally, to the scientifically minded rubber technologist it is an important factor in interrelating the numerous and otherwise isolated test results which are customarily reported.

The molecular theory of rubber elasticity [19] in its simplest form is based on the statistical mechanics of a freely jointed network chain involving no internal energy changes. This leads to the well-known equation

$$W = \frac{NkT}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

where W = elastically stored free energy, N = number of network chains per unit volume; k = Boltzmann constant; T = absolute temperature; and λ_1, λ_2, λ_3 = principal extension ratios.

This equation is often written in the simpler form

$$W = \frac{G}{2}(I_1 - 3)$$

where $G = NkT = \rho RT/M_c = 2\nu RT$; ρ = density; R = gas constant; M_c = molecular weight between crosslinks; ν = number of crosslinks per unit volume; and $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ (the so-called first strain invariant).

The stress is given by

$$\sigma = \frac{dW}{d\epsilon}$$

where ϵ is the strain. In the case of simple extension this yields the familiar equation

$$\sigma = G(\lambda - \lambda^{-2})$$

where λ = simple extension ratio.

In the case of solvent-swollen rubbers this becomes

$$\sigma = Gv_r^{1/3}(\lambda - \lambda^{-2})$$

where v_r is the volume fraction of rubber in the swollen material.

Although the form of the above stress-strain equation for swollen rubbers is observed (for small deformations) it does not describe the behavior of unswollen rubbers at all well. Also, when independent methods for evaluating the chemical crosslink density became available [10] it was observed that there was generally a discrepancy between the crosslink density determined by chemical analysis and by application of the stress-strain equation even in swollen rubbers. This latter discrepancy could be explained partly by the inevitable entanglements of interpenetrating network chains, which behaved as crosslinks, and partly by the presence of elastically ineffective chain ends which are a result of a finite molecular weight of the rubber molecules [20].

The discrepancy between theory and experiment in unswollen rubbers is more serious. The problem is not so much to think of reasons for the discrepancies as to select from the large number of possibilities those which are significant, and also amenable to rigorous mathematical treatment. There is a further problem in that while limited experimental observations may appear to verify a particular theoretical refinement, more extensive observations (for example, those involving more general strains than that of simple extension) often do not. Many attempts have been made to refine the statistical theory and these are dealt with admirably in the second edition of Prof. Treloar's now classic book [21].

The phenomenological theory of rubber elasticity [22] in its most general form, is based only on the symmetry requirements of strain energy with respect to the independent strain variables for an isotropic material. The strain invariants are:

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

$$I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2\lambda_1^2$$

$$I_3 = \lambda_1^2\lambda_2^2\lambda_3^2$$

In this general form the strain energy is given by the functional equation

$$W = f(I_1, I_2, I_3)$$

from which

$$\sigma\, d\epsilon = dW = \frac{\partial W}{\partial I_1}dI_1 + \frac{\partial W}{\partial I_2}dI_2 + \frac{\partial W}{\partial I_3}dI_3$$

If $\partial W/\partial I_2 = 0$, $\partial W/\partial I_1 = \text{constant}$, and $dI_3 = 0$ (no volume change), the equation reduces to the simple kinetic theory form.

If $\partial W/\partial I_1$ = constant (C_1), $\partial W/\partial I_2$ = constant (C_2), and $dI_3 = 0$, the equation reduces to

$$dW = \sigma \, d\epsilon = C_1 dI_1 + C_2 dI_2$$

which in simple extension becomes

$$\sigma = C_1 \frac{dI_1}{d\lambda} + C_2 \frac{dI_2}{d\lambda}$$

or

$$\frac{\sigma}{2}(\lambda - \lambda^{-2})^{-1} = C_1 + C_2\lambda^{-1}$$

This is the well-known Mooney-Rivlin equation and by plotting experimental values of $\sigma/2\,(\lambda - \lambda^{-2})^{-1}$ as a function of λ^{-1} a straight line of slope C_2 and intercept C_1 should be obtained. In practice, a straight line is observed with values of λ between about 1.3 and 2.5. Moreover the value of C_1 (when corrected by $v_r^{1/3}$) is virtually independent of the degree of swelling and is thus identified with G/2 of the kinetic theory.

Unfortunately, in general strain, C_2 cannot be regarded as constant and other forms of the I_2 part of the stored energy function describe the elastic behavior much better [23]. However, the new value of the equivalent term to C_1 thus obtained gives a value for the degree of crosslinking which varies widely with the volume of swelling by solvents.

The Mooney-Rivlin equation is therefore still widely used to measure the degree of crosslinking, in spite of the experimental deviations (especially in homogeneous uniaxial compression). The assumption that rubber is incompressible ($dI_3/d\epsilon = 0$) is not strictly true and $\partial W/\partial I_3$ may be the missing term required to provide a stored energy function which would give both a sensible value for the crosslink density and describe the general elastic behavior well. Unfortunately the form of $\partial W/\partial I_3$ at large strains is difficult to establish, either theoretically or experimentally.

Since the C_2 term has no place in the simple kinetic theory and as normally measured is probably an experimental repository of other terms (including strain-induced volume changes and filler effects due to insoluble extra-network material) interpretation of the significance of changes in C_2 with changes in curing systems is difficult. Such changes do occur and will be discussed in later sections.

As there is no independent method for determining crosslink density, changes in C_1 must be generally be interpreted as changes in the crosslink density. The only exception to this are (1) where insoluble extra-network material has a stiffening effect which can be removed by extraction with suitable solvents and (2) where soluble extra-network material has a softening effect (equivalent to swelling) which can also be removed by extraction. These are discussed later.

Finally there are various "non-equilibrium" contributions which influence the stress-strain relationships and which undoubtedly contribute to the C_2 term. These will be discussed under hysteresial properties.

CRYSTALLIZATION EFFECTS AT HIGH STRAIN

In noncrystallizing elastomers at high strains ($\lambda > 3.5$) departure from the simple kinetic theory of rubber elasticity is undoubtedly due to the finite extensibility of the rubber chains. An elegant theoretical treatment of this by Treloar [21] is available but the adjustment of parameters to fit observed curves is cumbersome particularly when non-affine effects are included (Fig. 5). In crystallizing elastomers the effect of finite chain extensibility merges with the effect of strain-induced crystallization, which makes interpretation difficult.

An empirical equation due to Martin, Roth, and Stiehler [24] gives a very good description of the stress-strain relationship for natural rubber in simple extension up to the point where crystallization effects come in.

This is of the form:

$$\ln \frac{\sigma\lambda^2}{\lambda - 1} = \ln E_0 + A(\lambda - \lambda^{-1})$$

where E_0 = Young's modulus at zero strain and A = constant (at constant temperature). For hysteresial rubbers the stress must be measured isochronally

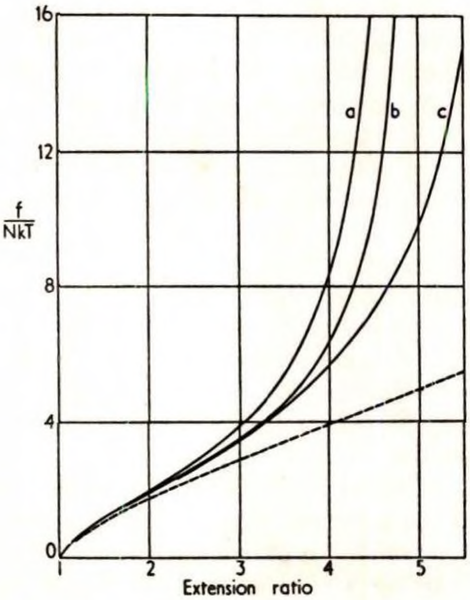

FIG. 5. Non-Gaussian force-extension curves for n = 25; (a) three-chain model; (b) tetrahedral model, affine displacement; (c) tetrahedral model non-affine displacement. (- - - -), Gaussian.

(equal times taken to stretch to each extension from zero). Although this equation lacks a theoretical basis and can only be used for simple extension (including uniaxial homogeneous compression) it provides a useful indication of the onset of strain-induced crystallization [25]. Around this onset of crystallization the straight-line relationship between ln $\sigma(\lambda^2/\lambda - 1)$ and $\lambda - \lambda^{-1}$ undergoes an abrupt increase of slope (Fig. 6). This has been identified [25] with an abrupt change in the differential Young's modulus due to the filler stiffening effect of the crystallites and can be related to a differential strain amplication [25] factor $\dot{X}$.

The extension ratio (λ_c) at which this change of slope occurs decreases with increase in crosslink density, whereas at constant crosslink density it increases in the order peroxide < EV < high-sulfur vulcanizates (Fig. 6). This is in accord with the known ranking order of the times for crystallization to occur at low temperature. The $\dot{X}$ factor decreases in the order peroxide > EV > high-sulfur vulcanizates, which is also in agreement with the low-temperature crystallization rates. These results are summarized in Table III.

Recent X-ray diffraction data also give agreement about the ranking order of λ_c, but rank degrees of crystallization just above λ_c in a reverse order to that which might be inferred from stress-strain $\dot{X}$ values. This may reflect the

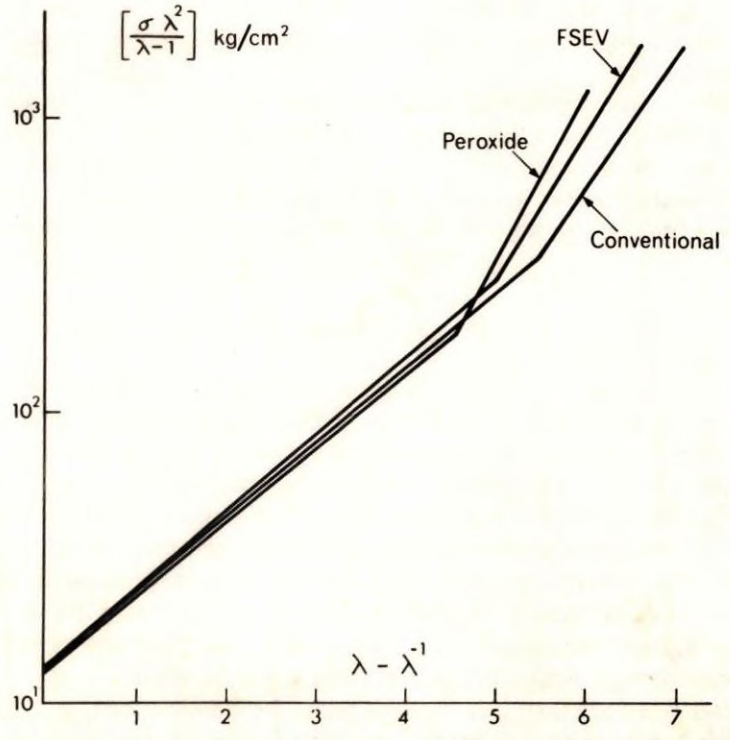

FIG. 6. Stress-strain relationships in extension, plotted according to the Martin, Roth, and Stiehler equation, of different types of natural rubber vulcanizates having the same crosslink density.

TABLE III

Variation of A_0, λ_c, and $\dot{X}$ with Type of Vulcanizate
at Constant Crosslink Density

	Peroxide	Soluble-EV	Conv.
E_0, kg cm^{-2}	13.0	13.3	13.1
C_1, kg cm^{-2}	2.03	1.97	1.92
A_0, kg cm^{-2}	0.66	0.61	0.59
λ_c	4.86	5.24	5.72
$\dot{X}$	2.26	2.19	2.08

existence of significantly different crystallite morphologies in the different vulcanizates, or merely difficulties in the interpretation of X-ray diffraction intensities.

INELASTIC PROPERTIES

The kinetic theory of rubber elasticity is based on equilibrium considerations and does not cover inelastic behavior. In the deformation of real rubbers there are inelastic contributions to observed stresses which are of considerable practical importance.

Certain useful properties of elastomers, such as wet friction, strength, and resonance damping in vibration isolators, depend on inelasticity in a very positive way, albeit under very different conditions of frequency and strain. Other undesirable properties, such as creep, stress relaxation, and heat build-up are also manifestations of the inelastic component of rubber deformation behavior.

The Glass Transition

There are a number of contributions to the inelastic behavior of rubber which depend, in varying degrees, on temperature, frequency (or time scale), strain, and polymer structure. The most dramatic of these, and hence the most thoroughly studied, is the phenomenon of the glass transition.

The flexibility of long-chain molecules is largely a function of the ease of rotation of constituent atoms about the chemical bonds which link them along the chain. This in turn depends on the rotational energy barriers and interchain attractive forces. At sufficiently high temeprature, and providing the time scale is sufficient, these barriers become insignificant. At low temperatures, however, the thermal energy is insufficient for the polymer molecules to adopt their *equilibrium configuration in sympathy with deformation, and the material* behaves as a rigid glass. The precise temperature at which the transition from rubberlike to glasslike state takes place is frequency- (or time-scale) dependent, but under standard conditions of measurement is well-defined and is known as the glass- or second-order transition temperature.

Just as the pressure-volume-temperature properties of liquids and gases can largely be reduced to a common pattern by using the critical values as reference points, so also can the mechanical properties of polymers be largely reduced to a common pattern by using the glass-transition temperature as a reference [26]. In spite of its success this approach is only approximate and becomes less reliable as conditions move away from the glass transition. Other mechanisms of inelastic behavior then assume greater relative importance.

The glass-transition temperature of an elastomer is normally well below the temperature of the environment in which it is used. Only properties involving very high deformation frequencies, such as sliding friction, approach the glass-transition condition [27].

Simple crosslinking increases the glass-transition temperature of a polymer, but at the levels normally used in elastomers the effect is very small [28]. Probably of greater importance is the amount of main-chain modification introduced during vulcanization with sulfur. The glass transition of a natural rubber derivative consisting entirely of cyclic sulfide repeat units is unknown but is probably very high ($\gg$100°C).

Modifications at the more normally observed levels are (presumably) distributed randomly along the chain, so that as well as slightly increasing the glass-transition temperature, they would also be expected to produce a significant broadening of the peak. This indeed seems to be the case in sulfur vulcanizates containing a moderate level of main-chain modification (Fig. 7).

Inelastic Behavior Due to Chemical Change

At sufficiently high temperatures an apparent loss of elasticity is caused by chemical changes in the network taking place during elasticity measurements. These processes may be chemically irreversible and are then the same as those involved in aging but have special consequences since they occur in the deformed condition.

Chemically reversible reactions, such as crosslink interchange, can also take place, and whereas they would not be detected by ordinary aging measurements, they are readily observed in deformed rubber—by stress relaxation, for example. In practice, both types of chemical change take place simultaneously.

Polysulfidic crosslinks are particularly labile at high temepratures and, in vulcanizates where they predominate, they lead to high rates of stress relaxation, creep, and set (Fig. 8).

Intermediate Temperatures

In protected natural rubber peroxide vulcanizates the difference between the glass-transition temperature (-70°C) and the temperature at which chemical changes begin (100-150°C) is very large. The more restricted temperature range of most service applications (ca -20°C to +60°C) is well removed from either of these extremes and normally compounded peroxide vulcanizates are almost perfectly elastic over this range. (An exception to this is that at the lower temperatures crystallization of the rubber eventually

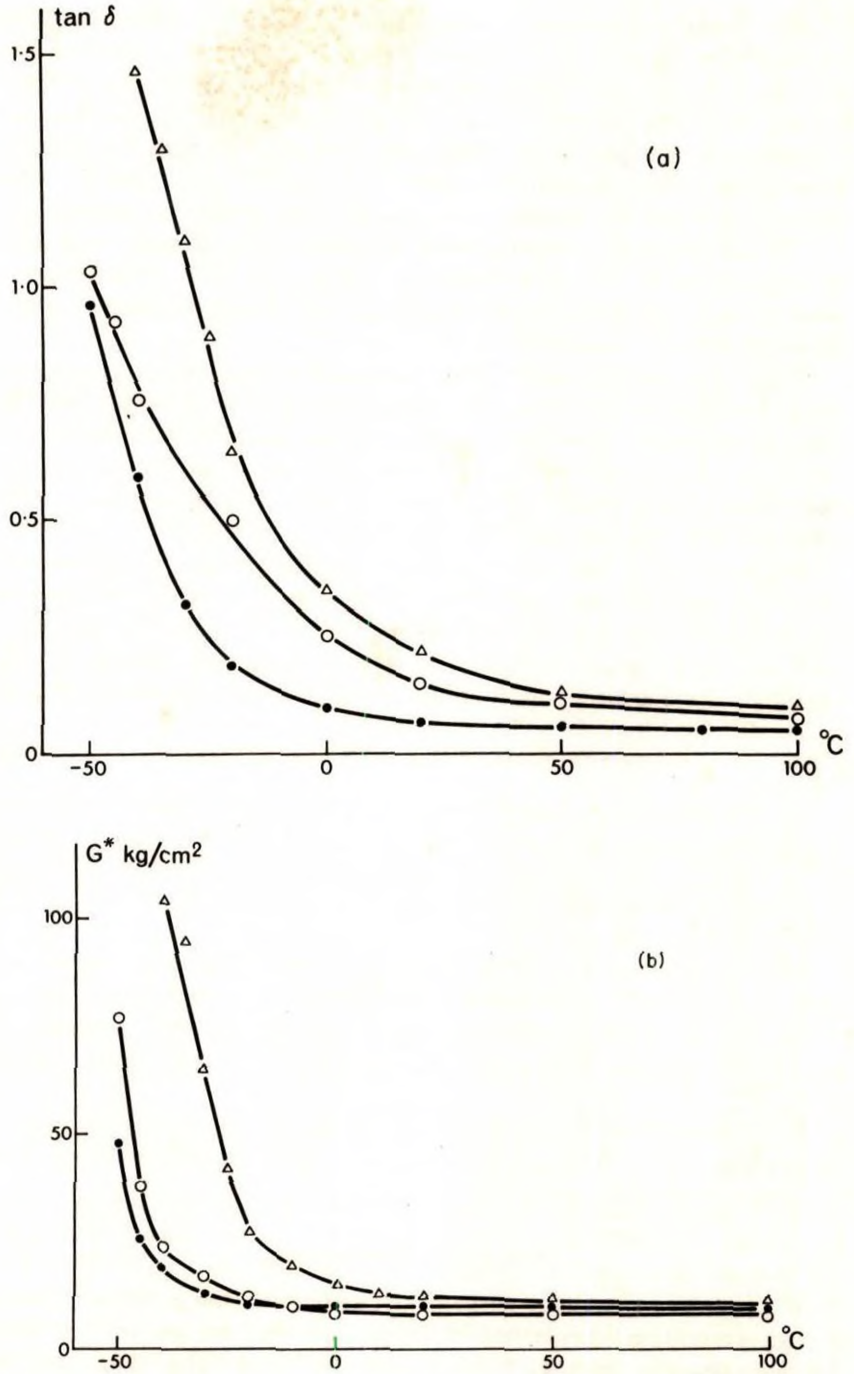

FIG. 7. *Effect of temperature on stiffness.* (●), Natural rubber/fully soluble EV formulation; (○), natural rubber/conventional accelerated sulfur formulation; (△), polychloroprene. (a) Loss factor (tan δ), (b) complex modulus (G*).

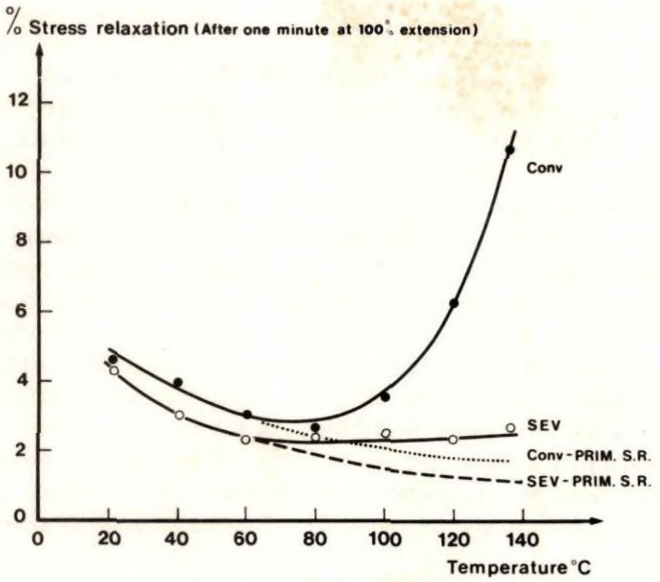

FIG. 8. The effects of temperature and curing system on the stress relaxation occurring during the first minute after extension of deproteinized natural rubber vulcanizates. CONV = conventional system (S, 2.6; CBS, 0.6 pphr) with 1 pphr stearic acid, 1.5 pphr BLE 25, and 35 pphr HMF black; cured for 30 min. at 140°C. SEV = soluble EV system (S, 0.84; MOR, 2.04; TBTD, 0.84 pphr) with 0.5 pphr zinc 2-ethyl hexanoate, 1.5 pphr BLE 25, and 35 pphr HMF black; cured for 90 min. at 140°C. PRIM. S.R. ≈ primary stress relaxation.

occurs.) Conventional sulfur vulcanizates of natural rubber have a still small though significantly greater tendency to inelastic behavior, in this intermediate range.

Zinc Soap Effects

The main cause of the significantly greater inelastic behavior of sulfur vulcanizates compared with those of peroxide vulcanizates was eventually traced [29] to the structurization within the former of the zinc soaps formed from the fatty acids normally used in the compound (usually stearic acid).

Zinc stearate, and indeed most other zinc soaps of straight chain fatty acids, have high melting points (ca. 130°C) and are very insoluble in rubber. By contrast zinc soaps of branched chain, alicyclic, or otherwise modified fatty acids are viscous liquids and comparatively soluble in rubber. Substitution of stearic acid by one of these acids (or often more conveniently by the corresponding zinc soap) leads to a significant increase in the elastic behavior of sulfur vulcanizates, which, particularly in the case of EV systems, is then comparable with that of peroxide vulcanizates. A dramatic reduction in stress relaxation in the intermediate temperature range (primary stress relaxation) is observed (Fig. 9), probably because of the comparatively long time scale involved in such measurements.

Conventional vulcanizates contain main-chain modifications and have somewhat higher primary stress relaxation rates (Fig. 9), due probably to the chain stiffening effect of the modifications, as referred to earlier in the section on glass transition.

The marked reduction of primary stress relaxation rates of sulfur vulcanizates containing rubber-soluble zinc soaps suggested that the envisaged simple mechanism (time-dependent deformation of soap micelles when insoluble zinc soap is present) was correct. Further experiments using solvent extractions have, however, shown that the mechanism is more complex, and involves interactions with rubber-bound carboxylic acid groups [4, 30] (Fig. 10). The origin of these bound carboxylic acid groups, which are present only in small quantities, raises interesting questions. They may arise from covulcanization of unsaturated natural fatty acids with the rubber. Such an effect can indeed be demonstrated with linoleic acid [30] which is the major acid consistuent naturally present [31]. However, the effect observed when

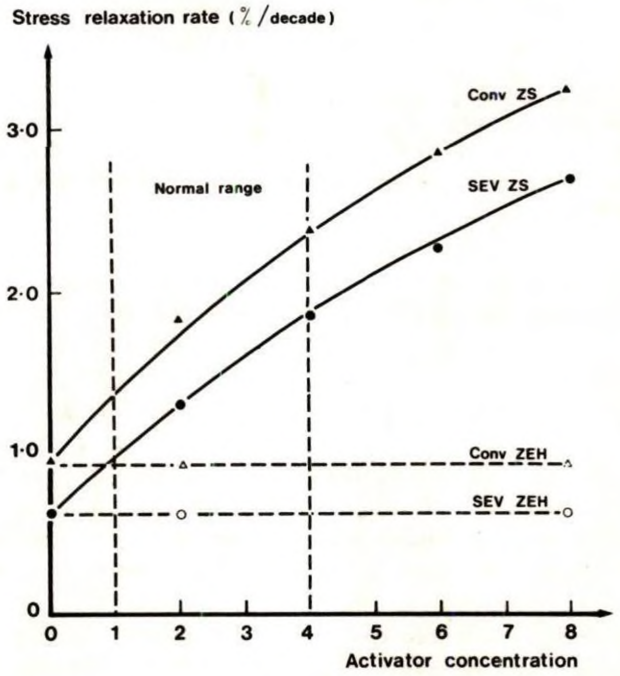

FIG. 9. The effects of activator concentration and curing system on the rate of primary stress relaxation at 30°C of NR gum vulcanizates (SMR5CV). Conv ZS = conventional system (S, 2.5; CBS, 0.6 pphr), with zinc stearate activator. Conv ZEH = conventional system (S, 2.5; CBS, 0.6 pphr), with zinc 2-ethyl hexanoate activator. SEV ZS = soluble EV (S, 0.7; MOR, 1.7; TBTD, 0.7 pphr), with zinc stearate activator. SEV ZEH = soluble EV (S, 0.7; MOR, 1.7; TBTD, 0.7 pphr), with zinc 2-ethyl hexanoate activator. The modulus (MR100) of all vulcanizates was 0.73 MNm^{-2}. The activator concentration is expressed as the chemically equivalent stearic acid concentration in pphr.

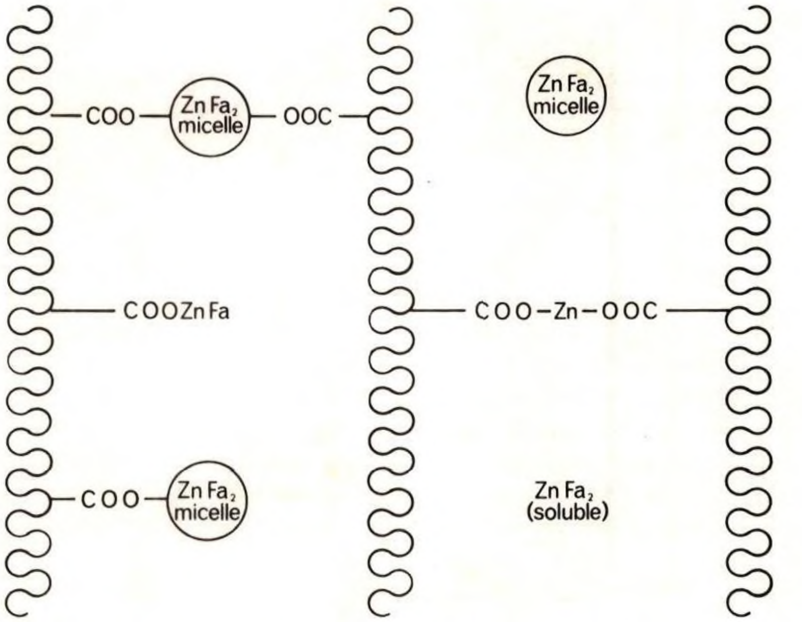

FIG. 10. Schematic representation of network-bound and extra-network zinc soap molecules and micelles.

linoleic acid is added to purified rubber accounts for only about one-tenth of that observed in commercial grades of natural rubber. The presence of a small amount of a much more reactive unsaturated fatty acid is possible and might account for this difference.

An alternative possibility follows recent observations of the seasonal variations of the ratio of $C_1{}^{14}$ acetate to $C_2{}^{14}$ acetate incorporated during rubber biosynthesis [32]. The most obvious fate of the anomalous excess $C_1{}^{14}$ acetate which occurs at certain times is as side-chain carboxylate groups.

Strain Effects on Stress Relaxation

The effect of extension on the stress relaxation rate of efficient sulfur vulcanizates at 30°C is shown in Figure 11. The zinc soap effect is seen to be largest at small strains and the curve shape in this region can be explained by assuming that the relaxation due to soap is mainly in the C_2 term of the Mooney–Rivlin equation. This is also consistent with the close linear correlation between the increase in C_2 and the stress relaxation rate at 100% extension (Fig. 12).

The marked increase in the stress relaxation rate at strains between 100% and 300% has been attributed to rubber crystallization, but the fact that the normal kinetic form $(\Delta \log \sigma)/(\Delta \log t) = \text{constant}$ for primary stress relaxation is maintained at these strains is not in accord with this. The irreversibility due to non-affine network deformation seems a more likely explanation.

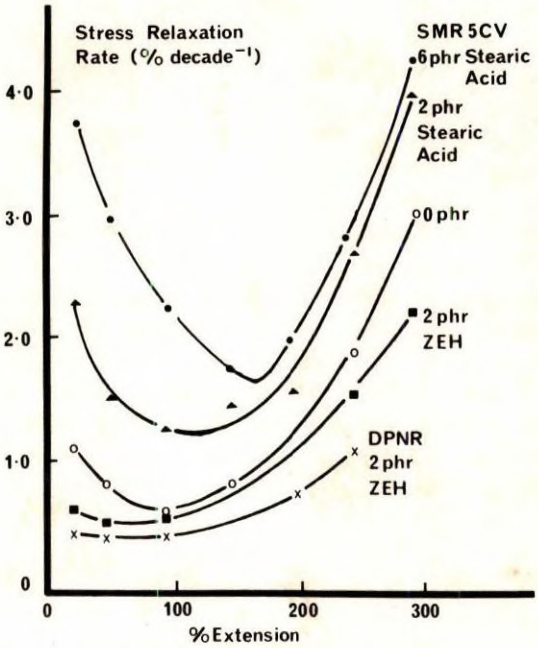

FIG. 11. Variation of stress relaxation with strain for various levels of soluble and insoluble activators in soluble-EV gum natural rubber vulcanizates. ZEH = zinc 2-ethyl hexanoate, DPNR = deproteinized natural rubber.

Effects of Degree of Crosslinking

Most of the measures of inelastic behavior (stress relaxation, phase angle, resilience, hysteresis ratio, dynamic/static modulus ratio, stress softening, set) are functions of the ratio of loss modulus/storage modulus. Since the storage modulus of an elastomer is profoundly dependent on the degree of crosslinking, so also will these parameters be. Comparisons of such parameters using different curing systems should therefore be made at equal degrees of crosslinking or storage modulus (Fig. 13).

STRENGTH PROPERTIES

The strength properties of an elastomer are of obvious technological importance. They are also among the most difficult of properties to interpret in fundamental terms. This is largely due to the high and inhomogeneous strain conditions around a growing crack. This is particularly complicated in the case of natural rubber in which strain-induced crystallization is a major factor.

The fracture mechanics approach has unified the results [33] from different test pieces and has been successful in explaining the significance of the fatigue limit of mechanical cut growth under cyclic relaxing deformation.

At higher strains the fatigue life becomes more difficult to interpret, in molecular terms, by fracture mechanics, partly due to the incursion of hysteresial effects (for which a precise theoretical treatment is very difficult) and partly due to changes of uncertain origin in the crack condition. An alternative phenomenological approach [34] demonstrates the powerful influence of hysteresis on strength but, we believe, requires the development of a sounder theoretical basis.

The strength of an elastomer may be expressed in a variety of related ways including the peak values of tearing energy, work of deformation, tensile stress, or tensile strain. Whichever form is adopted, the value will depend on temperature, number of cycles to failure, mean strain, effective flaw size (except for tearing energy, the measurement of which requires the effective flaw size to be known), and the frequency of deformation. In natural rubber the frequency of deformation has a relatively small effect. Any study of the influence of curatives (or indeed of any compounding or processing changes) which ignores these variables, can provide only a very restricted viewpoint.

Tensile Strength

The tensile strength may be regarded as a limiting case of fatigue in which failure occurs in half an extension cycle. It is clearly far removed from conditions near the fatigue limit. Nevertheless the tensile strength is of considerable interest and importance.

There are two complications which can obscure the effects of network structure on tensile strength: moulding anisotropy and "spotty" inhomogeneous vulcanization due to crystallication pre-growth of poorly soluble curatives (including sulfur) [35]. The effects can be avoided by careful

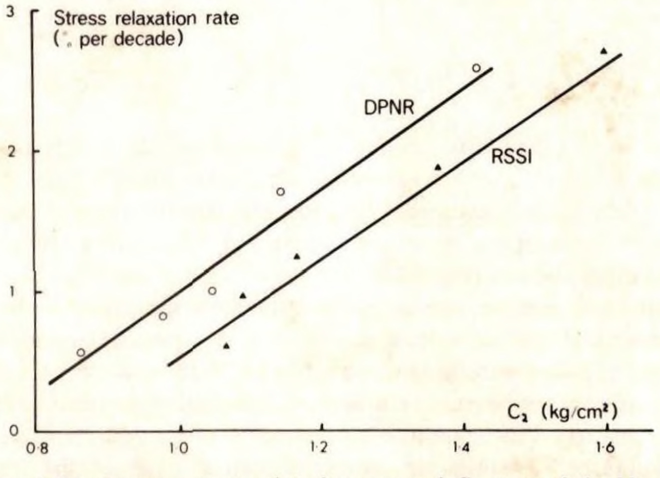

FIG. 12. Correlation between stress relaxation rate and C_2 term of the Mooney–Rivlin equation for vulcanizates of deproteinized natural rubber (DPNR) and ribbed smoked sheets (RSS1).

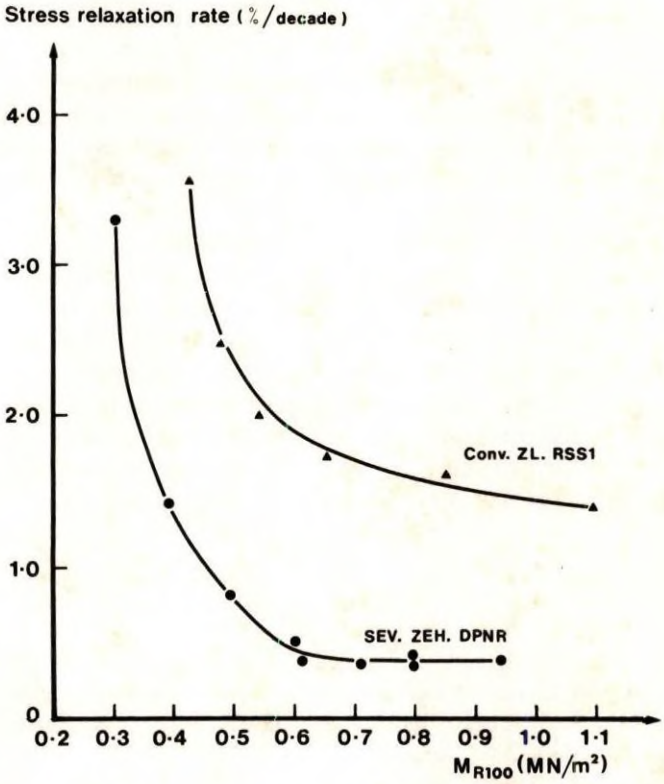

FIG. 13. The effect of degree of crosslinking on the primary stress relaxation rates of natural rubber vulcanizates. The relaxed modulus at 100% extension was varied by changing the curative levels (keeping the sulfur to accelerator ratios constant) and is used as the indication of degree of crosslinking. CONV.ZL.RSS1 = conventional accelerated sulfur vulcanizates with 2 pphr of lauric acid using RSS1. SEV.ZEH.DPNR = soluble EV vulcanizates with 2 pphr of zinc 2-ethyl hexanoate using deproteinized natural rubber.

processing (pre-pressing at 100°C for about 30 min.) and choice of soluble levels of curatives.

Recent work [25a] has extended the temperature range of tensile strength measurements on a range of vulcanizates with known structural differences and has clearly demonstrated the positive contribution of polysulfidic crosslinks to the strength of natural rubber and the negative contribution of main-chain modifications (Fig. 14).

The effect of temperature is particularly interesting in that the work to break for natural rubber vulcanizates shows two peaks, around 60°C and -35°C (Fig. 15). Comparison with SBR (data shifted to correct the difference in glass-transition temperatures) indicates that both the peaks with natural rubber are due to crystallization, but presumably of two different types.

The influence of polysulfic groups is seen throughout the temperature range, but is much larger with natural rubber than with SBR. It is not clear whether the influence of $-S_x-$groups is due to crosslink lability or to changes in crystallite morphology and efforts are being made to resolve this [25a].

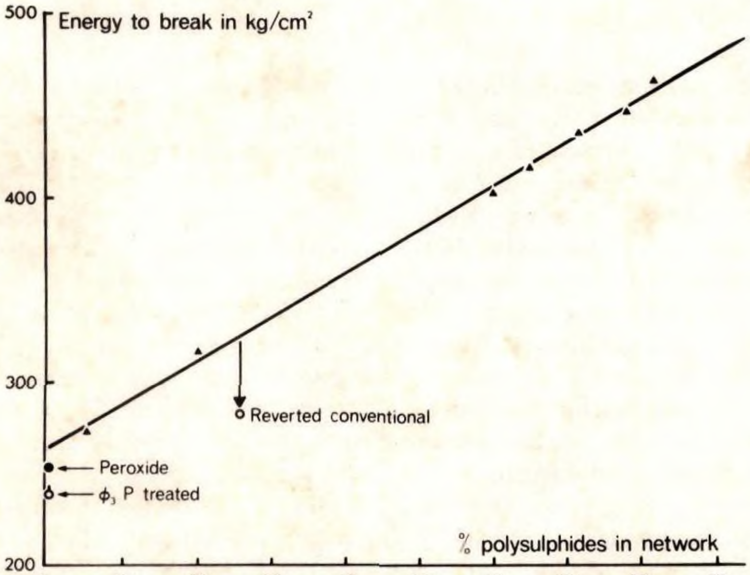

FIG. 14. Effects of structural features of the vulcanizate on the strength of natural rubber.

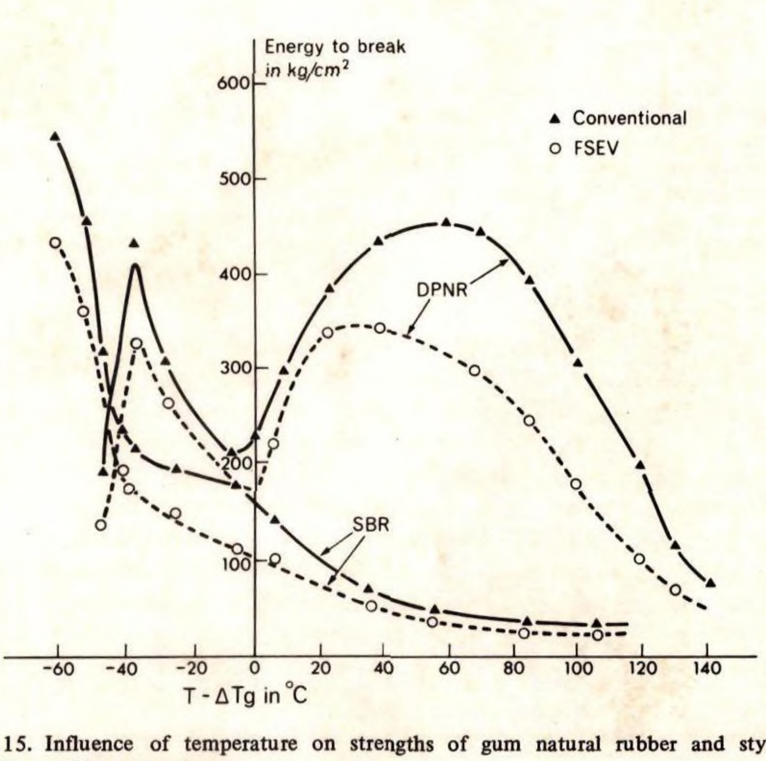

FIG. 15. Influence of temperature on strengths of gum natural rubber and styrene-butadiene rubber vulcanizates.

Fatigue

The measurement of fatigue properties involves a large number of variables and takes a lot of experimental time, especially as conditions approach the fatigue limit. The subject is covered elsewhere in this symposium [33], and only a few broad features will be mentioned here.

Mechanical cut growth, under static deformation conditions, does not normally occur with natural rubber, due presumably to strain-induced crystallinity [36]. However, excessive main-chain modification and excessive degrees of crosslinking do make natural rubber susceptible to this type of failure.

The mechanochemical fatigue limit of natural rubber under relaxing dynamic conditions is, by contrast, slightly lower than that of noncrystallizing polymers and can be increased by main-chain modification [37]. There is a dramatic increase in the dynamic fatigue life of natural rubber as the superimposed mean static strain is increased [38] (Fig. 16).

Under relaxing conditions the fatigue life of natural rubber vulcanizates containing essentially polysulfidic crosslinks is significantly (two to three times) better than that of vulcanizates with mono- and disulfidic or carbon-carbon crosslinks. These differences disappear under nonrelaxing conditions. At high temperatures, and depending on the strain severity, simultaneous aging of the rubber takes place and profoundly alters these generalizations.

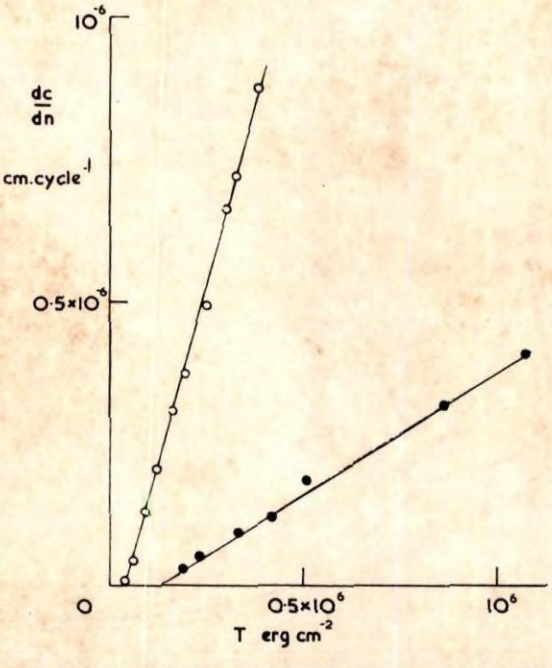

FIG. 16. Cut growth behavior of natural rubber in relaxing and nonrelaxing cycle fatigue experiments in the laboratory atmosphere. (○), Complete relaxation allowed; (●), nonrelaxing experiment (ratio of minimum to maximum tearing energy of cycle = 0.056).

CONCLUSIONS

The effect of different curing systems on natural rubber properties is comparable in magnitude with differences between polymers. Many of the effects can be related to differences in network structure, but extra-network materials can also profoundly affect the aging and long-term hysteresial behavior. Strain-induced crystallization is an important but complicating feature of the high strength of natural rubber vulcanizates.

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