

Structural Characterization of Vulcanizates. Part V. Determination of Degree of Chemical Crosslinking of Natural Rubber Gum Vulcanizate Networks

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Synopsis

A general treatment is given of the methods to be used in other parts of this series for calculating the degree of chemical crosslinking in natural rubber vulcanizates from stress-strain measurements in extension and from equilibrium volume swelling measurements. Corrections are required for the presence in the vulcanizate of appreciable quantities of particulate solids or soluble diluents and for the introduction of foreign atoms into the rubber network. For this purpose distinction is made between the rubber vulcanizate, the rubber matrix, the rubber network, and the rubber hydrocarbon component of the network. Expressions are derived, in terms of these concepts, for the Mooney-Rivlin parameter, C_1 , measured on vulcanizates which have undergone various treatments.

INTRODUCTION

The crosslinking of rubber molecules to form a three-dimensional network is normally carried out in the presence of considerable quantities of added materials (fillers, extending oils, curatives, ancillary substances, etc.). Such materials may be in solution in the rubber at the time of crosslinking, in which case the network is formed in a swollen state, or they may be present as insoluble particles, which contribute to the modulus of the vulcanizate. The presence of both types of material must, in general, be taken into account in determining the degree of crosslinking of the network from the equilibrium volume swelling or stress-strain properties of the vulcanizate.

In a gum vulcanizate the amounts of extra-network substances present are usually so small (ca. 5 vol.-%) that their effects on swelling and stress-strain properties are not greatly in excess of experimental error; they are therefore often neglected. However, work to be described in subsequent parts of this series (Parts VI and VII)^{1,2} has involved the preparation of gum vulcanizates of natural rubber which contain larger (10-20 vol.-%) quantities of nonrubbers, the effects of which on physical properties are no longer negligible. In making determinations of degrees of chemical crosslinking in these vulcanizates we have applied corrections to take into account the presence of this material. While the bases for some of these corrections are

still partly subject to experimental verification, we believe that they are the best at present available, and in order to make fair comparison between vulcanizates of different types it has been considered desirable to apply the corrections even in cases in which they are comparable in magnitude to experimental error. The resulting unified method of treatment for natural-rubber gum vulcanizates is described in full in this paper in order to simplify the presentation of results in subsequent parts of this series.

RELATIONSHIP BETWEEN DEGREES OF PHYSICAL AND CHEMICAL CROSSLINKING

The relationship between the physically manifested degree of crosslinking, $(2M_{c, \text{phys}})^{-1}$, and the degree of chemical crosslinking, $(2M_{c, \text{chem}})^{-1}$, of a natural-rubber vulcanizate network deduced by Mullins^{3,4} and Moore and Watson⁵ is of the following form:

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

dyne cm.⁻² at 25°C. (1)

in which $C_{1, \text{RH}}$ is the experimentally determined value of the elastic parameter C_1 of the Mooney-Rivlin equation, referred to the rubber hydrocarbon component of the network, ρ_{RH} is the density (0.915 g./ml. at 25°C.) of "natural rubber hydrocarbon" (defined in the following section), \bar{M}_n is the number-average molecular weight of the raw rubber, determined by measurement of the intrinsic viscosity in benzene and application of the relationship⁶ $[\eta] = 2.29 \times 10^{-7} \bar{M}_n^{1.33}$, $M_{c, \text{chem}}^{\text{RH}}$ is the number-average molecular weight of the rubber hydrocarbon component of the chain segments between physically effective chemical crosslinks in the network, R is the gas constant, and T is the absolute temperature.

This relationship refers to networks which contain essentially only the atoms present in the original rubber. Correction for the increase in the mean molecular weight of a chain segment due to combination of foreign atoms (usually sulfur) in the crosslinks or in groups attached to the main polymer chains was made in Part I⁷ by correcting values of $(2M_{c, \text{chem}}^{\text{RH}})^{-1}$, that is, after the relationship eq. (1) had been applied. On logical grounds we now prefer to apply a correction to C_1 before using eq. (1); see pp. 2219-2220.

Two qualifications regarding the accuracy of eq. (1) need to be made. First, Bristow et al.⁸ recently observed that the stoichiometry of crosslinking of natural rubber by di-*t*-butyl peroxide depends on the type of rubber used, whether it is extracted before vulcanization or not, and on the concentration of peroxide. They concluded that the efficiency of crosslinking, in Moore and Watson's experiments, on which eq. (1) is based,⁵ was probably less than 100% and that some revision of eq. (1) is therefore necessary.

Second, in the work on which eq. (1) is based the values of the elastic constant C_1 and of the volume fraction of rubber in the swollen gel at equilibrium swelling, v_r , pertained to vulcanizates which had been extracted with

n-decane and which were therefore slightly "supercoiled" or "collapsed" relative to the equilibrium state at which they were prepared. The extent of this supercoiling will have been small, since it is related to the volume of extra-network material dissolved in the rubber during the vulcanization process, and this will have consisted of small amounts only of di-*t*-butyl peroxide, *t*-butyl alcohol, acetone, etc., together with any material extractable from the raw deproteinized crêpe used. Although it is possible to express a C_1 value measured on any vulcanizate in the same way, it would not be correct to use such a value to derive the degree of chemical crosslinking of the network, since the extent of supercoiling will vary with the amount of network-soluble nonrubbers present in the vulcanizate; it is preferable to express all C_1 values relative to the unsupercoiled network, i.e., the network as prepared. In principle, this would require a small correction of the relationship expressed in eq. (1), so that it also would refer to an unsupercoiled network. There appears to be little merit in making this correction in practice, since its magnitude is less than 2.5% of C_1 , which is to be compared with both the experimental error in the measurement of C_1 itself (ca. 2% C_1) and the possible deficiency, referred to above, in the relationship between the physical and chemical degrees of crosslinking. In the following treatment and in subsequent parts of this series C_1 values have therefore been expressed relative to a normal (not supercoiled) network and eq. (1) has been applied. A simple correction only of the derived $(2M_{c, \text{chem}}^{\text{RH}})^{-1}$ values will therefore be required, if and when subsequent revision of the crosslinking relationship, eq. (1), is made.

DETERMINATION OF THE ELASTIC PARAMETER $C_{1, \text{RH}}$

Two methods have been in general use for the determination of the physically manifested degree of crosslinking, $(2M_{c, \text{phys}})^{-1}$, in vulcanizates: stress-strain measurements in simple extension and equilibrium volume swelling measurements.

Under conditions of routine evaluation natural-rubber vulcanizates conform to the behavior predicted by the statistical theory of rubberlike elasticity only under very limited conditions. Thus, eq. (2), in which f is the force required to extend a sample of the vulcanizate of unstrained cross-sectional area A_0 to an extension ratio λ , is obeyed only when the vulcanizate is highly swollen and then only over a limited extension range, since effects believed to be due to finite extensibility of the network chains begin to intrude at quite low extensions.^{4,9}

$$f = \rho RT A_0 M_{c, \text{phys}}^{-1} (\lambda - \lambda^{-2}) \quad (2)$$

The behavior of unswollen (dry) vulcanizates over a much larger range of extensions is described adequately¹⁰ by the Mooney-Rivlin equation, eq. (3), in which C_1 and C_2 are elastic parameters characteristic of the vulcanizate. C_1 has been identified³ with $\rho RT (2M_{c, \text{phys}})^{-1}$.

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

Values of C_1 are obtained in practice by extrapolation to $\lambda^{-1} = 0$ of the linear sections of plots of $f[2A_0(\lambda - \lambda^{-2})]^{-1}$ versus λ^{-1} , and such values are now preferred to those obtained from measurements on highly swollen samples,⁹ although it has usually been considered desirable, when investigating a new series of vulcanizates, to verify that values of C_1 for dry and swollen vulcanizates are in close parity by making measurements on a few representative vulcanizates in the partially swollen condition (see p. 2221).

The value of C_1 obtained by application of eq. (3) will, in general, vary somewhat with any pretreatment the sample may have received, such as solvent extraction for the removal of unreacted curative and ancillary agents or acid treatment for the removal of metal oxides and sulfides. These variations will usually not be large but may be so if, for example, appreciable quantities of nonreinforcing fillers or extending oils have been used in the preparation of the vulcanizate.

In establishing a standard procedure for applying corrections to C_1 values measured on variously treated samples in order to obtain the appropriate value ($C_{1,RH}$) for substitution in eq. (1) we have found it necessary to distinguish among the following:

- (1) *The rubber vulcanizate (RV)*, the vulcanizate as prepared.
- (2) *The rubber matrix (RM)*, that part of the vulcanizate containing the rubber network diluted by any rubber-soluble material present at the time of crosslinking but excluding any particulate solids (which are deemed to act as fillers).
- (3) *The rubber network (RN)*, the network formed from the rubber hydrocarbon and the curative by the vulcanization process, including any atoms or groups introduced in crosslinks or as modifications of the main rubber chains.
- (4) *The rubber hydrocarbon component of the network (RH)*; in the case of natural rubber it is appropriate to include not only *cis*-1,4-polyisoprene but also some 3 wt.-% of nitrogenous material (probably protein), which is not removed from peroxide vulcanizates of natural rubber by acetone extraction or ether-hydrochloric acid treatment¹¹ and is therefore essentially part of the rubber network; in the context of this series, therefore, rubber hydrocarbon is defined as that part of the raw rubber which is insoluble in hot acetone.

For the description of vulcanizates which have been extracted by a solvent or treated with an acid two further definitions are necessary:

(5) *An extracted rubber vulcanizate (ERV)*, a vulcanizate from which all rubber-soluble extra-network materials (including sol rubber) have been extracted, and which therefore consists of filler and a rubber network supercoiled to some extent.

(6) *An extracted rubber matrix (ERM)*, a vulcanizate from which all rubber-soluble extra-network materials have been extracted, and from which solid particles such as zinc oxide and zinc sulfide have been removed (usually by treatment with an acid); it is thus a supercoiled rubber network.

The parenthetical abbreviations in the definitions given above are used subsequently as subscripts to define various physical quantities with reference to the definitions; for example, $C_{1,ERV}$ is the C_1 value of a solvent-extracted vulcanizate, and V_{RN} is the volume fraction of rubber network in a vulcanizate.

Determination of $C_{1,RH}$ from Stress-Strain Measurements on Unswollen, Unextracted Vulcanizates

(1) Stress-strain measurements are made at temperatures close ($\pm 5^\circ\text{C}$.) to 25°C . for convenience and in order to avoid the necessity for a correction for thermal expansion. The C_1 values so obtained are corrected to 25°C . by means of the expression

$$C_{1,RV} = C_1 [\text{measured at } t^\circ\text{C.}] \times 298/(273 + t) \text{ dyne cm.}^{-2} \quad (4)$$

(2) Correction of $C_{1,RV}$ for the stiffening effect of nonreinforcing particulate fillers is made by means of the Guth and Gold relation:¹²

$$C_{1,RM} = C_{1,RV}(1 + 2.5V_f + 14.1V_f^2)^{-1} \quad (5)$$

where V_f is the total volume fraction of fillers in the rubber vulcanizate. In this context the term "fillers" includes any extra-network material present in the vulcanizate as solid particles. For gum sulfur vulcanizates of natural rubber it generally comprises free elemental sulfur in excess of the equilibrium solubility concentration of about 1 wt.-% at room temperature, zinc oxide, zinc sulfide, and zinc mercaptides of accelerators (e.g., zinc benzothiazolyl mercaptide, zinc dimethyldithiocarbamate), if the latter are not rendered soluble by complex formation with amines or zinc carboxylates. Zinc carboxylates appear not to act as fillers when present in conventional amounts (up to 4 wt.-% of the vulcanizate); much larger amounts (ca. 10–15 wt.-%) may lead to unusual stress-strain behavior in the vulcanizate.^{1,2}

Although eq. (5) was derived for low concentrations of spherical particulate fillers, there is good evidence that it is applicable to a wide range of nonreinforcing and lightly reinforcing fillers in the concentration range 0–0.1 in V_f (up to 39% correction of $C_{1,RV}$).^{13–17}

When only one filler is present in a vulcanizate, V_f is best calculated from the weights W and densities ρ of the filler and vulcanizate:

$$V_f = W_f \rho_{RV} / W_{RV} \rho_f \quad (6)$$

With several different solid species V_f is more easily calculated from the composition of the vulcanizate, when this is known.

(3) The C_1 value of the rubber matrix, $C_{1,RM}$, is corrected on a simple volume basis for the presence of soluble extra-network materials and of network-combined atoms introduced during the crosslinking process:

$$C_{1,RH} = C_{1,RM} \times (1 - V_f) / V_{RH} \quad (7)$$

V_{RH} , the volume fraction of rubber hydrocarbon in the vulcanizate, refers to that part of the *raw* natural rubber which is not soluble in hot acetone [cf. definition (4) above] and is obtained similarly to V_f above. For this calculation it is necessary to know the proportion of rubber hydrocarbon present in the original mix which is not combined in the rubber network, i.e., the proportion of sol rubber. This is not readily determined for vulcanizates containing appreciable quantities of extra-network materials, and in later parts of this series the absence of sol rubber has generally been assumed. The error in $C_{1,RH}$ due to this assumption is about 1% for a vulcanizate with $C_1 \approx 1.1 \times 10^6$ dyne cm.⁻² and about 3% for one with $C_1 \approx 0.5 \times 10^6$ dyne cm.⁻².

Determination of $C_{1,RH}$ from Stress-Strain Measurements on Unswollen, Extracted Vulcanizates

This section refers to vulcanizates which have been extracted with a suitable solvent so that only the filler and the supercoiled rubber network remain.

(1) The measured C_1 is corrected to 25°C. as on p. 2219.

(2) The value of $C_{1,ERV}$ so obtained is corrected for the stiffening effect of the remaining particulate solids:

$$C_{1,ERM} = C_{1,ERV}[1 + 2.5 V_f' + 14.1(V_f')^2]^{-1} \quad (8)$$

in which V_f' is the volume fraction of filler in the extracted vulcanizate.

(3) $C_{1,ERM}$ refers to a rubber network free from extraneous material but supercoiled relative to its state when prepared. So far as we are aware, the effect on stress-strain properties of swelling agents present at the time of cure and subsequently removed by extraction has not been investigated experimentally. However, an expression may be derived¹⁸ by considering the effect of diluent present during crosslinking on the root-mean-square distance between the ends of a chain in the unstrained state, r_0 , and on the number of molecular chains between crosslinks per unit volume, N , in the stress-strain relation for simple extension given by the statistical theory of rubberlike elasticity:

$$f = A_0 k T r_0^2 n^{-1} l^{-2} (\lambda - \lambda^{-2}) \quad (9)$$

in which k is Boltzmann's constant, l is the length of a random link, and n is the number of such links in a molecular chain. The derived expression is:

$$C_{1,RM} = C_{1,ERM} \times V_{RN}^{1/2} / (1 - V_f)^{1/2} \quad (10)$$

where V_{RN} and V_f refer to the volume fraction of rubber network and filler, respectively, in the *untreated* rubber vulcanizate. V_{RN} is obtained either directly by treatment of the extracted vulcanizate with ether-hydrochloric acid or indirectly by calculation if the composition of the vulcanizate is known. Combination with eq. (7) then gives:

$$C_{1,RH} = C_{1,ERM} \times V_{RN}^{1/2} (1 - V_f)^{1/2} / V_{RH} \quad (11)$$

**Determination of $C_{1,RH}$ from Stress-Strain
Measurements on Unswollen, Extracted Vulcanizates
Treated with Ether and Hydrochloric Acid**

After extraction with a suitable solvent and treatment with a hydrochloric acid-ether mixture¹⁹ an accelerated natural-rubber-sulfur vulcanizate consists essentially of a supercoiled network. Stress-strain measurements on such a vulcanizate therefore give $C_{1,ERM}$ directly, from which $C_{1,RH}$ can be obtained using eq. (11).

**Determination of $C_{1,RH}$ from Stress-Strain
Measurements on Swollen Vulcanizates**

This section refers to vulcanizates swollen *after* cure.

Although highly swollen vulcanizates in simple extension more nearly conform to statistical theory [eq. (2)] than do dry rubbers, the intrusion of finite extensibility effects at low extensions tends to give artificially high C_1 values. Values determined on dry rubbers have therefore been preferred. Nevertheless, in dealing with a new series of vulcanizates it is considered desirable to confirm the reliability of C_1 values made on dry vulcanizates by making measurements on a representative number of partially swollen vulcanizates. Since the swelling procedure removes some, but not necessarily all, of the extra-network material, the prior removal of the latter by solvent extraction is recommended.

It is convenient to derive the value of C_1 appropriate to the corresponding unswollen vulcanizate directly by plotting

$$fL[2A_{0,swollen}(\lambda - \lambda^{-2})]^{-1} \quad \text{or} \quad f[2A_{0,dry}L(\lambda - \lambda^{-2})]^{-1}$$

against λ^{-1} , where L is the ratio of the swollen length to the unswollen length of the sample.⁹ The C_1 value so obtained can be corrected for the effect of nonreinforcing fillers by the Guth-Gold equation (8), in which V_f' now refers to the volume fraction of fillers in the swollen vulcanizate (for many conventional vulcanizates this correction is very small and may often be ignored). This gives a value of $C_{1,ERM}$, which may then be compared with $C_{1,ERM}$ measured on a dry vulcanizate (p. 2220). Alternatively, stress-strain measurements may be made on a vulcanizate swollen after extraction and ether-hydrochloric acid treatment, in which case $C_{1,ERM}$ is obtained directly.

**Determination of $C_{1,RH}$ from Equilibrium
Volume Swelling Measurements**

The equilibrium degree of swelling attained by a rubber network in a swelling agent is related to the physically manifested degree of crosslinking, $(2M_{c,phys})^{-1}$, by the Flory-Rehner equation,²⁰ eq. (12), or by the modified equation,²¹ eq. (13):

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = \rho V_0 M_{c,phys}^{-1} v_r^{1/3} \quad (12)$$

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = \rho V_0 M_{c,phys}^{-1} (v_r^{1/3} - v_r/2) \quad (13)$$

in which v_r is the volume fraction of rubber network in the swollen gel at equilibrium, V_0 is the molar volume of the swelling agent, and χ is a parameter characteristic of interaction between the rubber network and swelling agent. While there is theoretical preference for the modified eq. (13), in the absence of experimental verification we have preferred to use the simpler original form, eq. (12), with the further advantage that the values of χ derived are less dependent upon v_r (cf., e.g., Bristow²²).

Since a volume swelling measurement is made with reference to a vulcanizate which does not contain inert fillers, i.e.,

$$v_r = (\text{volume of rubber network}) / [(\text{total swollen volume}) - (\text{volume of filler})] \quad (14)$$

the expression of eq. (12) in terms of the Mooney-Rivlin treatment of rubber elasticity gives

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = 2V_0 C_{1, \text{RM}} / LRT \quad (15)$$

In the equilibrium state, when virtually all soluble extra-network material has been leached out by the swelling agent, the denominator of eq. (14) is equivalent to the volume of the rubber network plus the volume of the solvent imbibed or, in terms of previously defined volume fractions,

$$v_r = V_{\text{RN}} / [V_{\text{RN}} + (\text{vol. solvent}) / (\text{vol. unextracted vulcanizate})]$$

V_{RN} is found as described on p. 2220. L , the linear extension ratio of the vulcanizate on swelling (p. 2221), is given by the expression

$$\begin{aligned} & [(\text{tot. swollen vol.} - \text{vol. filler}) / (\text{vol. unextracted vulc.} - \text{vol. filler})]^{1/2} = \\ & [(\text{vol. solvent} + \text{vol. network}) / (\text{vol. unextracted vulc.})]^{1/2} \times \\ & [1 / (1 - V_f)^{1/2}] = V_{\text{RN}}^{1/2} / v_r^{1/2} (1 - V_f)^{1/2} \end{aligned}$$

Combining eq. (15) with eq. (10) gives

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = 2V_0 C_{1, \text{ERM}} v_r^{1/2} / RT \quad (16)$$

This result also follows directly from eq. (12), since v_r necessarily refers to a supercoiled network when soluble material is present during crosslinking. Finally, in terms of $C_{1, \text{RH}}$,

$$-\ln(1 - v_r) - v_r - \chi v_r^2 = (2V_0 C_{1, \text{RH}} / RT) [V_{\text{RH}} v_r^{1/2} / V_{\text{RN}}^{1/2} (1 - V_f)^{1/2}] \quad (17)$$

In the special case in which no filler is present ($V_f = 0$) and no new atoms become attached to the rubber during the crosslinking process ($V_{\text{RH}} \equiv V_{\text{RN}}$) the term $V_{\text{RH}} / V_{\text{RN}}^{1/2} (1 - V_f)^{1/2}$ becomes $V_{\text{RN}}^{1/2}$, giving the form of correction for crosslinking in the presence of a diluent deduced by Flory.²¹

Use of eq. (17) with the Mullins relation, eq. (1), allows determination of the degree of chemical crosslinking from equilibrium volume swelling measurements, if the value of χ appropriate to the particular vulcanizate net-

work and swelling agent is known. Alternatively, χ may be obtained by measurement of $C_{1,ERM}$ and v_r , or of $C_{1,RM}$ and L and substitution in eq. (16) or (15), respectively.

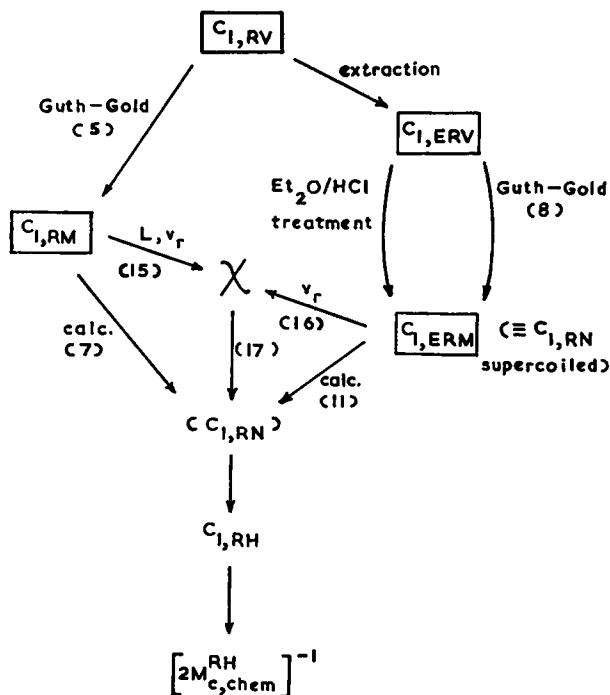


Fig. 1. Relations between various C_1 parameters, χ , and degree of chemical crosslinking. Boxed quantities are directly accessible experimentally; figures in parentheses refer to equations in the text.

The relations between the various C_1 parameters and the derivation of $(2M_{c,chem}^{RH})^{-1}$ from them are summarized schematically in Figure 1.

DETERMINATION OF CROSSLINKING EFFICIENCY

The efficiency E of utilization of sulfur for crosslinking is defined as the number of sulfur atoms combined in the vulcanizate network per physically effective chemical crosslink formed. In the work to be described in later parts of this series organically combined sulfur, $[S_c]$, is determined as the difference between the sulfur remaining, $[S_c + S^{2-}]$, after extraction of the vulcanizate with a solvent, under conditions which ensure the removal of free sulfur and sulfur-containing reaction products not bound to the network, and inorganic sulfide sulfur $[S^{2-}]$ determined on the unextracted vulcanizate, due allowance being made for the proportion of material extracted. Values of $[S_c]$ so obtained are converted to the form appropriate for the calculation of values of E ($= [S_c](2M_{c,chem}^{RH})$) by the formula

$[S_c]$ (g.-atom per g. RH in network) =

$$\frac{S_c \text{ (wt.-% unextracted vulc.)} \times \text{wt. mix containing 100 g. raw rubber}}{3206 (100 - \% \text{ acetone extract of raw rubber})}$$

Values of F , the number of molecules of zinc sulfide formed per physically effective chemical crosslink, are obtained analogously from S^{2-} data.

MAGNITUDE OF CORRECTIONS

For conventional gum vulcanizates of natural rubber the magnitude of the total correction involved in deriving C_1 referred to the rubber hydrocarbon component of the network, $C_{1,RH}$, from a C_1 measurement on an untreated vulcanizate, $C_{1,RV}$, is in the range 0–5%. A correction of similar magnitude is required when $C_{1,RH}$ is derived from $C_{1,ERM}$ as obtained from equilibrium volume swelling data. Hence, for this type of vulcanizate the corrections are not large relative to the possible error in the crosslinking calibration [eq. (1)] and are, in fact, comparable to the experimental errors. In less conventional vulcanizates, such as those treated in Part I,⁷ in which appreciable amounts of sulfur are combined in the network, and those discussed in Part VI,¹ which contain considerable amounts of extra-network material in the form of zinc laurate, the corrections are larger. For the vulcanizates of Part I the total correction lies in the range –8 to +6%, depending on initial sulfur concentration and reaction time, whereas for those of Part VI a correction of +15% is necessary.

The arguments developed here necessitate some correction of the results of Parts I,⁷ II,²³ III,²⁴ and IV,¹⁹ of this series. As stated already, in Part I account was taken of the increase in the mean molecular weight of the chain segment, due to combined sulfur, in deriving values of $(2M_{c,chem}^{RH})^{-1}$ from stress-strain data, although not in the way described above. Treatment of the data of Part I by the present methods leads to values of $(2M_{c,chem}^{RH})^{-1}$ which are 0–5% larger than those given, and crosslinking efficiencies E will therefore be reduced by similar amounts. The main conclusions of Parts I and II are not affected by these changes.²³

Amendment of the derived degrees of chemical crosslinking for the natural rubber and *cis*-1,4-polyisoprene systems of Parts III²⁴ and IV¹⁹ is very minor ($\approx 2\%$) except for the "efficient" systems accelerated by 2-mercaptobenzothiazole and *N*-cyclohexylbenzothiazole-2-sulfenamide (cf. Tables IV and V of Part IV). In these cases the published degrees of chemical crosslinking should be increased by 10–13%, and values of the crosslinking efficiency before and after triphenylphosphine treatment (E and E' , respectively) should be similarly reduced. These two systems are therefore even more efficient than is apparent from the published data (cf. Parts VI¹ and VII²).

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Résumé

On donne un traitement général des méthodes à utiliser, dans d'autres articles de cette série pour calculer le degré de pontage chimique dans les vulcanisats de caoutchouc naturel au départ de mesures de tension-déformation en extension et au départ de mesures de gonflement à l'équilibre. Certaines corrections sont rendues nécessaires par la présence dans le vulcanisat de quantités appréciables de particules solides ou de diluants solubles et par l'introduction d'atomes étrangers dans le réseau caoutchouteux. A cet effet, on fait la distinction entre le vulcanisat de caoutchouc, la matrice du caoutchouc, le réseau du caoutchouc et le composant hydrocarboné du caoutchouc dans le réseau. Sur la base de ces concepts, on déduit des expressions pour le paramètre de Mooney-Rivlin, C_1 , mesuré sur des vulcanisats qui ont subis différents traitements.

Zusammenfassung

Eine allgemeine Behandlung der in anderen Teilen dieser Reihe zur Berechnung des chemischen Vernetzungsgrades von Naturkautschukvulkanisaten aus Spannungs-Dehnungsmessungen und aus Quellungsgleichgewichtsmessungen anzuwendenden Methoden wird gegeben. Korrekturen sind für die Gegenwart beträchtlicher Mengen von Feststoffen, die als Partikel auftreten, oder löslicher Verdünnungsmittel in den Vulkanisaten und für die Einführung von Fremdatomen in das Kautschuknetzwerk

erforderlich. Zu diesem Zweck wird zwischen dem Kautschukvulkanisat, der Kautschukmatrix, dem Kautschuknetzwerk und der Kautschukkohlenwasserstoffkomponente des Netzwerks unterschieden. Mit diesem Konzept werden Ausdrücke für den an Vulkanisaten nach verschiedenartiger Behandlung gemessenen Mooney-Rivlin-Parameter, C_1 , abgeleitet.

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