

Determination of Degree of Crosslinking in Natural Rubber Vulcanizates. Part III.

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I. INTRODUCTION

The two previous parts of this series^{1,2} described an attempt to relate the physical properties of natural rubber vulcanizates to their network structure. The first established an empirical relationship between the stress-strain behavior of highly swollen natural rubbers in simple extension, and their equilibrium volume swelling in *n*-decane. It also examined the effect of changes in initial molecular weight of the unvulcanized masticated rubber on these properties, and an empirical correction making allowance for network flaws due to chain-segments terminated by a crosslink at only one end was obtained. The second part² gave measurements of the equilibrium volume swelling and the intrinsic viscosity before vulcanization for each of a range of natural rubber vulcanizates which had been prepared by a method which enabled the number of crosslinks to be determined by chemical analysis. These measurements permitted a comparison to be made between (i) the chemical estimate of the actual number of crosslinks introduced and (ii) the number derived from the data on equilibrium volume swelling, by means of the empirical relations derived in Part I. For this purpose, an assumption was made that the stress-strain behavior of highly swollen rubbers was in accord with the predictions of the statistical theory.

Recent studies^{3,4} of both the stress-strain properties of highly swollen rubbers and the method of determining number-averaged molecular weight from intrinsic viscosity measurements have provided an improved basis for the quantitative determination of the degree of crosslinking from measurements of physical properties. The results described in Parts I and II of this series are reinterpreted here to take account of both of these developments; in addition, the effect of the introduction of a correction for a network defect equivalent to chain entanglements is examined.

II. MODIFIED BASIS FOR DETERMINATION OF PHYSICAL DEGREE OF CROSSLINKING

Stress-Strain Behavior of Highly Swollen Rubbers

Previous investigations^{1,5} have shown that the stress-strain behavior of both dry and swollen rubber in simple extension can be described by an expression of the form suggested by Mooney⁶ and Rivlin,⁷

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

where C_1 and C_2 are parameters characterizing the vulcanizate and the degree of swelling, and f is the force required to extend a sample of rubber of unstrained cross-sectional area A_0 to an extension ratio λ . The value of C_2 was shown to decrease progressively as the degree of swelling was increased until at high degrees of swelling it became exceedingly small and the dependence of force on deformation was then given by

$$f = 2 A_0(\lambda - \lambda^{-2})C_1 \quad (2)$$

and thus followed the predictions of the statistical theory.

Recent studies³ in which stress-strain measurements have been examined up to higher extensions have shown that departures from the simple form of stress-strain curves given by eqs. (1) and (2) occur at large extensions. These are due to the finite extensibility of the network chains. With dry rubbers, these departures only became important at large extensions but with highly swollen rubbers, they were present at much lower elongations. Under these conditions they made the determination of accurate values of C_1 extremely difficult, and resulted in an increase in the apparent value of C_1 and a decrease in the apparent value of C_2 determined by plotting $1/2fA_0^{-1}(\lambda - \lambda^{-2})^{-1}$ against λ^{-1} .

It was shown that values of C_1 varied with swelling in the manner predicted by the statistical theory and that the value of $C_1v_r^{1/2}$ remained inde-

pendent of degree of swelling until, with highly swollen rubbers, these departures due to finite extensibility became significant at low elongations. Thus in this investigation, values of C_1 determined on dry rubbers are used to characterize the network structure. The use of values of C_1 determined on dry rubbers instead of swollen rubbers as previously results in a decrease in the estimated degree of crosslinking by approximately 10%.

Determination of Initial Molecular Weight

Mullins and Watson³ have recently redetermined the limiting viscosity number-molecular weight relationship for samples of masticated natural rubber and have obtained the following expression

$$[\eta] = 2.29 \times 10^{-7} M^{1.33} \quad (3)$$

TABLE I
Relationship between C_1 and v_r
(Measurements at $25 \pm 0.2^\circ\text{C}$.)

Vulcanizate	$M^{-1} \times 10^6$	C_1 , dynes- cm. ⁻² $\times 10^{-6}$	C_2 , dynes- cm. ⁻² $\times 10^{-6}$	v_r
A 1	4.57	1.08	0.70	0.253
2	5.60	1.07	0.75	0.242
3	7.00	0.93	0.63	0.227
4	7.75	0.82	0.54	0.213
5	10.05	0.75	0.47	0.201
B 1	4.60	1.53	0.86	0.285
2	5.70	1.63	0.83	0.292
3	6.40	1.62	0.78	0.292
4	9.20	1.22	0.63	0.259
5	11.20	0.77	0.46	0.213
C 1	6.00	1.10	0.72	0.250
2	7.60	1.02	0.70	0.240
3	9.50	0.85	0.52	0.225
4	11.10	0.72	0.42	0.211
D 1	4.95	1.85	0.87	0.308
2	6.20	1.80	0.80	0.303
3	7.35	1.75	0.78	0.299
4	9.00	1.59	0.72	0.293
5	11.75	1.50	0.65	0.279
E 1	4.80	1.79	0.88	0.304
2	4.80	1.50	0.83	0.283
3	4.80	1.43	0.79	0.277
4	4.80	0.99	0.71	0.238
5	4.80	0.70	0.68	0.204
6	4.80	0.61	0.56	0.192
F 1	3.10	1.85	1.01	0.314
2	3.95	1.90	0.94	0.314
3	5.12	1.86	0.87	0.313
4	7.05	1.67	0.78	0.302
5	9.65	1.57	—	0.292
H 1	4.20	1.37	0.93	0.271
2	6.00	1.30	0.91	0.273
3	6.50	1.22	0.81	0.265
4	7.20	1.18	0.80	0.265

which is somewhat different from that previously employed.⁸

The use of the new relationship for the determination of initial molecular weight makes little difference to the *absolute* value of the empirical correction to be applied for chain ends.

Both of these modifications have been introduced into the previous results.

(i) Relationship between C_1 and v_r

The first step was to provide a new relationship between C_1 and v_r using values of C_1 determined from stress-strain measurements made on *dry* samples of rubber at 25°C . and measurements of their equilibrium volume swelling in *n*-decane at 25°C . Measurements were made on all the samples examined in Part I following the procedures described there.¹ Compounding details and vulcanization procedures are given in the Appendix. The results obtained on the peroxide vulcanizates are given in Table I and are shown graphically in Figure 1. Here the value of C_1 is plotted as ordinate and the corresponding value of v_r for equilibrium volume swelling is plotted as abscissa.

The full line in the figure shows the theoretical relationship derived by Flory-Huggins^{10,11} to describe the dependence of equilibrium volume swelling on degree of crosslinking. The relation is

$$-\ln(1 - v_r) - v_r - \mu v_r^2 = \rho V_0 M_c^{-1} v_r^{1/3} \quad (4)$$

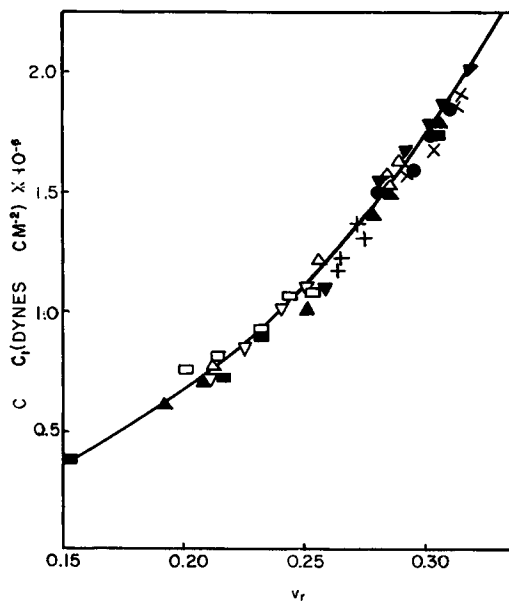


Fig. 1. Dependence of elastic constant C_1 on the equilibrium volume swelling v_r . (\square) A. (Δ) B. (∇) C. (\bullet) D. (\blacktriangledown) E. (\times) F. ($+$) H.

Assuming

$$C_1 = \frac{1}{2}\rho RTM_c^{-1} \quad (5)$$

a value⁵ of μ of 0.42 was found to give the best fit to the experimental results. This is to be compared with the value³ of μ of 0.41 determined in Part I.

(ii) Dependence of C_1 on Initial Molecular Weight

The empirical correction for the effect of initial molecular weight was redetermined using values of C_1 obtained on dry vulcanizates and introducing the modified relationship to obtain estimates of the number average molecular weight from intrinsic viscosity data.

The six series of rubbers A, C, D, F, H, and G provided vulcanizates which within each series had the same degree of crosslinking but were different in their initial molecular weights. Load-deformation measurements were made at 25°C. on dry samples of each of the vulcanizates and from them, values of C_1 and C_2 were determined. The results are given in Table II together with measurements

TABLE II
Effect of Change of Intrinsic Viscosity on C_1 and C_2

Vulcanizate	$[\eta]$, (g./100 ml.) ⁻¹	$M^{-1} \times 10^6$	C_1 , dynes-cm. ⁻² $\times 10^{-6}$	C_2 , dynes-cm. ⁻² $\times 10^{-6}$	
A	1	2.82	4.75	1.08	0.70
	2	2.30	5.60	1.07	0.75
	3	1.71	7.00	0.93	0.63
	4	1.48	7.75	0.86	0.54
	5	1.03	10.05	0.75	0.47
C	1	2.12	6.00	1.10	0.72
	2	1.52	7.60	1.02	0.70
	3	1.10	9.50	0.85	0.52
	4	0.91	11.10	0.72	0.42
	D	1	2.70	4.95	1.85
2		2.05	6.20	1.80	0.80
3		1.60	7.35	1.75	0.78
4		1.19	9.00	1.59	0.72
5		0.86	11.75	1.50	0.65
F	1	4.80	3.10	1.85	1.01
	2	3.63	3.95	1.90	0.94
	3	2.57	5.12	1.86	0.87
	4	1.69	7.05	1.67	0.78
	5	1.08	9.70	1.57	—
G	1	4.34	3.40	1.31	1.01
	2	3.16	4.35	1.30	0.91
	3	2.38	5.45	1.21	0.90
	4	1.22	8.85	1.02	0.78
	5	0.80	12.9	0.72	0.57
H	1	3.30	4.20	1.37	0.93
	2	2.12	6.00	1.30	0.91
	3	1.88	6.50	1.22	0.81
	4	1.64	7.20	1.18	0.80

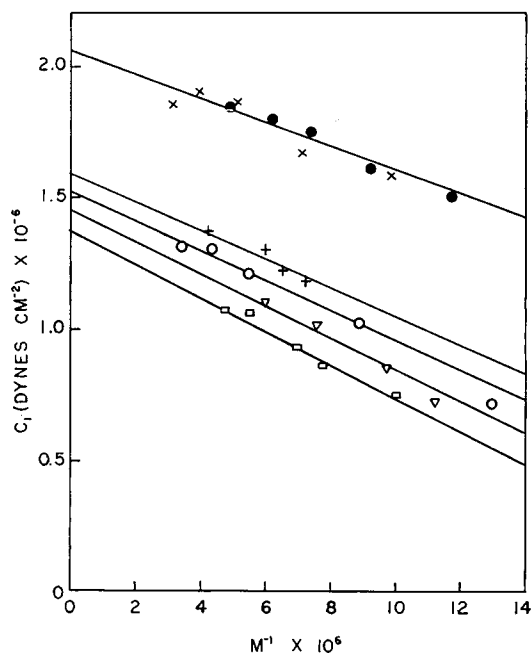


Fig. 2. Dependence of elastic constant C_1 on the reciprocal initial molecular weight M^{-1} .

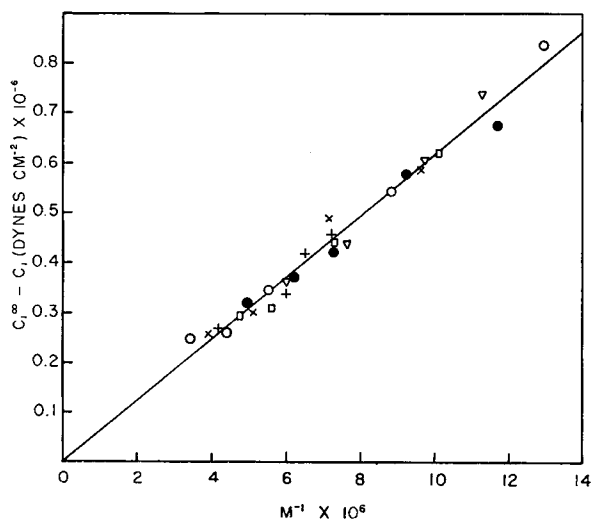


Fig. 3. Change in elastic constant C_1 with the reciprocal initial molecular weight M^{-1} .

of their intrinsic viscosity prior to vulcanization and estimates of the reciprocal initial molecular weights.

The dependence of C_1 on initial molecular weight shown graphically in Figure 2. It will be seen that all of the results can, as previously, be represented satisfactorily by a simple linear dependence of C_1 on M^{-1} , and that the correction for initial molecular weight can now be expressed in the form

$$C_1 = C_1^\infty - 6.2 M^{-1} \times 10^{10} \text{ dynes cm.}^{-2} \quad (6)$$

TABLE III
Chemical and Physical Determinations of Degree of Crosslinking

Sample no.	M_c^{-1} (chemical) $\times 10^6$	$M^{-1} \times 10^6$	v_r	C_1 , dynes-cm. $^{-2} \times 10^{-6}$	No correction for entanglements		Correction for entanglements	
					C_1^∞ , dynes-cm. $^{-2} \times 10^{-6}$	M_c^{-1} (physical) $\times 10^6$	C^∞ , dynes-cm. $^{-2} \times 10^{-6}$	M_c^{-1*} (physical) $\times 10^6$
1	3.14	5.35	0.214	0.78	1.13	10.06	0.39	3.45
2	3.42	5.70	0.199	0.66	1.01	8.99	0.36	3.20
3	3.44	5.70	0.144	0.62	0.97	8.63	0.33	2.95
4	3.58	5.35	0.219	0.81	1.14	10.15	0.44	3.90
5	3.94	5.35	0.227	0.89	1.22	10.86	0.48	4.25
6	4.84	5.35	0.240	1.02	1.35	12.02	0.57	5.10
7	4.92	5.35	0.241	1.03	1.36	12.10	0.58	5.15
8	5.74	5.35	0.252	1.14	1.47	13.08	0.66	5.85
9	5.76	5.65	0.246	1.08	1.43	12.73	0.63	5.60
10	6.34	5.70	0.248	1.10	1.45	12.91	0.66	5.85
11	6.46	5.70	0.249	1.11	1.46	12.99	0.67	5.95
12	10.16	5.70	0.293	1.68	2.03	18.07	1.15	10.20
13	10.20	5.70	0.294	1.69	2.04	18.16	1.16	10.30
14	14.76	5.33	0.333	2.25	2.58	22.96	1.75	15.60
21	2.20	5.65	0.172	0.47	0.82	7.30	0.28	2.50
22	3.62	5.35	0.211	0.75	1.08	9.61	0.40	3.55
23	5.16	5.35	0.237	0.98	1.31	11.66	0.55	4.85
24	6.10	5.33	0.261	1.24	1.57	13.97	0.60	6.70
25	6.66	5.65	0.257	1.19	1.57	13.97	0.73	6.45
26	12.94	5.33	0.326	2.15	2.48	22.07	1.58	14.05
28	4.40	5.35	0.232	0.93	1.26	11.21	0.51	4.50
29	5.52	5.35	0.248	1.10	1.46	12.99	0.64	5.65
30	7.52	5.33	0.262	1.25	1.58	14.06	0.76	6.80
31	11.98	5.33	0.306	1.83	2.16	19.22	1.27	11.30
32	15.96	5.33	0.341	2.38	2.71	24.12	1.80	16.00
33	4.02	5.35	0.229	0.91	1.24	11.04	0.49	4.35
34	6.66	5.30	0.257	1.19	1.51	13.44	0.70	6.25
35	7.46	5.33	0.275	1.40	1.73	15.40	0.89	7.95
36	11.18	5.33	0.306	1.83	2.16	19.22	1.27	11.30

where C_1^∞ refers to the extrapolated value for infinite initial molecular weight.

Figure 3 gives all of the results plotted to demonstrate this linear relationship between $C_1^\infty - C_1$ and M^{-1} .

III. COMPARISON BETWEEN PHYSICAL AND CHEMICAL DETERMINATIONS OF DEGREE OF CROSSLINKING

Table III gives results on all of Moore and Watson's vulcanizates whose degree of crosslinking fell in the range within which the relationship between equilibrium volume swelling and C_1 had been established. In addition to their data on the chemical determination of the degree of crosslinking and the equilibrium volume swelling, the table also includes a revised estimate of the initial molecular weight and values of C_1 determined from the equilibrium volume swelling measurements using the empirical relation established in Figure 1. The

table also includes estimates of C_1 corrected for the effect of chain ends using the correction described by eq. (6) together with values of M_c^{-1} (physical) determined using the assumption

$$C_1 = \frac{1}{2}\rho RTM_c^{-1} \text{ (physical)}$$

Values of M_c^{-1} (physical) determined in this way are plotted against the chemical determination of M_c^{-1} in Figure 4. As in Moore and Watson's earlier interpretation of the data, the physical estimate of M_c^{-1} is always greater than the chemical estimate.

A possible explanation of the difference between the two estimates, which has previously been discussed by the author² and by Bueche,¹² is that the network is subject to restraints other than those resulting from crosslinks. One such form of restraints would result from chain entanglements, which would impose configurational constraints and behave elastically as though they were cross-

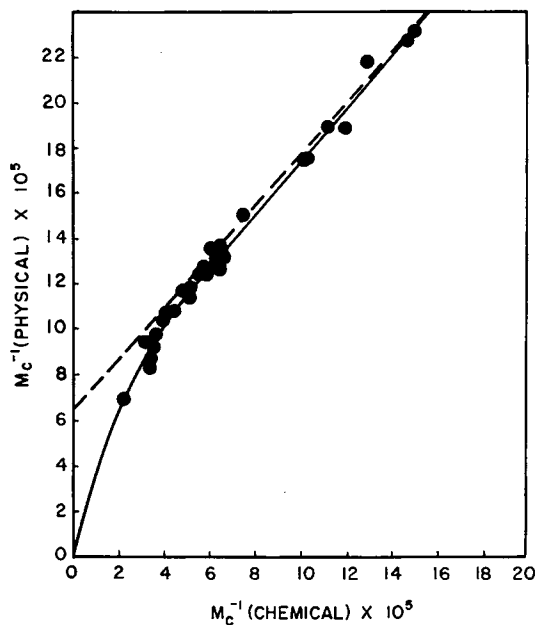


Fig. 4. Comparison of physical and chemical estimates of the reciprocal chain-segment molecular weight M_c^{-1} .

links. The consequences of the departures being due to entanglements are now further examined.

Corrections for the Contribution of Chain Entanglements

It is assumed that the measured value of C_1 contains a contribution due to chemical crosslinks and another due to chain entanglements acting as though they were crosslinks. It is further assumed that chain entanglements only contribute to the network if they are in chain-segments bounded by chemical crosslinks at both ends.

The contribution of entanglements to the total number of crosslinks will thus be greater the greater the fraction of rubber linked into the network, and with a highly crosslinked rubber or with rubber of high initial molecular weight, most of the potential entanglements will be effective as crosslinks. Thus in Figure 4, the intercept given by the extrapolation of the linear portion of the plot to zero degree of crosslinking gives an estimate of the maximum contribution of entanglements.

The correction for network flaws due to chain ends should be calculated not on the basis of the apparent number of crosslinks determined from C_1 , which includes both chemical crosslinks and entanglements, but on the basis of the *actual* number of chemical crosslinks. If the correction follows the forms shown by theoretical expressions^{13,14} and

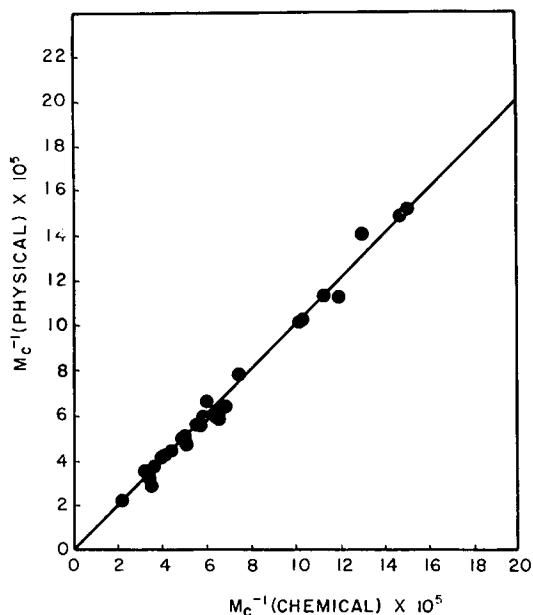


Fig. 5. Comparison of physical and chemical estimates of the reciprocal chain-segment molecular weight M_c^{-1} after allowance for chain-entanglements.

is linear with respect to $M_c M^{-1}$, then the number of effective crosslinks (N_e) will be given by the expression

$$N_e = (N_{\text{chemical}} + N_{\text{entanglements}}) \times (1 - \beta M_c M^{-1}) \quad (7)$$

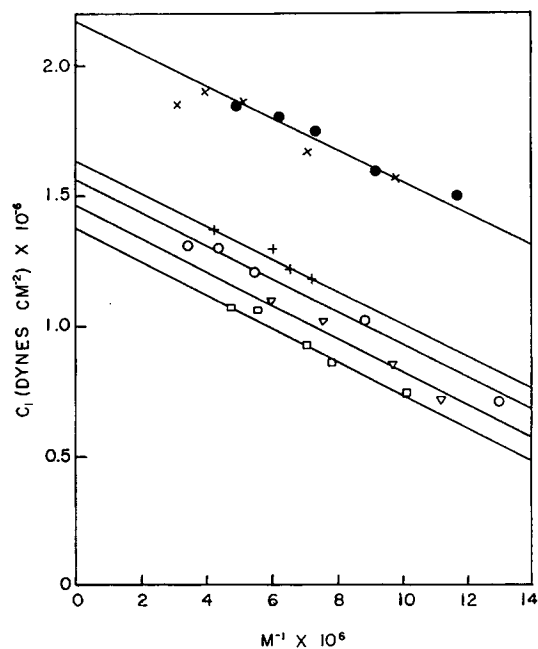


Fig. 6. Change in elastic constant C_1 with reciprocal initial molecular weight M^{-1} , using eq. (9).

where N entanglements is the maximum contribution of entanglements to the number of crosslinks, and M_c is the molecular weight of chain segment between adjacent chemical crosslinks. Or equivalently,

$$C_1 = (C_1^{\infty*} + \alpha)(1 - \beta M_c^* M^{-1}) \quad (8)$$

where α represents the maximum contribution of entanglements to C_1 , and M_c^* is now calculated from the new $C_1^{\infty*}$. Values of α and β were determined to fit the experimental results shown in Figures 2 and 4. The method used in this determination was one of successive approximations, and it was found that the relation between C_1 and initial molecular weight could be expressed by the relation

$$C_1 = (C_1^{\infty*} + 0.78 \times 10^6) \\ (1 - 2.3 M_c^* M^{-1}) \text{ dynes-cm.}^{-2} \quad (9)$$

Figure 5 shows the experimental data on the dependence of C_1 on initial molecular weight (previously given in Table II and shown in Figure 2) replotted; but now the full lines in the figure have been drawn using eq. (9). It will be seen that the experimental data can be just as well described by this new relation.

The last two columns of Table III give values of $C_1^{\infty*}$ and M_c^{-1*} (physical) derived from Moore and Watson's results and using the new empirical eq. (9) and assuming $C_1^{\infty*} = \frac{1}{2}\rho RT M_c^*$, and Figure 5 shows this new physical determination of M_c^{-1*} (physical) plotted against the chemical determination. The line in the figure has a slope of unity and there is now excellent agreement between the new physical estimate and the chemical estimate of M_c^{-1} .

It thus appears that when allowance is made for network flaws due to chain ends and chain entanglements by means of the two empirical corrections determined here, values of C_1 obtained in simple extension on either dry or swollen rubbers can be identified with the value predicted by the statistical theory, namely

$$C_1 = \frac{1}{2}\rho RT M_c^{-1}$$

This remarkable agreement between theory and experiment provides a most satisfactory confirmation of the relationship between the physical properties of rubber vulcanizates and their chemical structure.

At first sight this complete agreement must be regarded as fortuitous. The simple network model used as a basis for the statistical theory is obviously

an oversimplification, but it appears that, in simple extension, deviations from the theory at low and moderate extensions can be completely described by

- (i) an extra term in the stored energy function
- (ii) a correction for chain ends
- (iii) a correction for chain entanglements.

The only one of these three empirical corrections which has any theoretical basis is the correction for chain ends. The empirical correction closely corresponds to the theoretical correction developed by Flory¹³ which gives a value of $\beta = 2$, but it is now recognized that the network model used in Flory's determination of this correction is not completely realistic.¹⁶ It must also be recognized that the three empirical corrections are not independent and that a more refined analysis may alter their relative magnitudes. However, it is considered that the results indicate the general pattern of their contributions to stress-strain properties.

Further theoretical developments may modify the form of the appropriate stored energy function, but it appears unlikely that any simple statistical theory term in a new stored energy function will depart considerably from the value given by the first term in the Mooney-Rivlin form of stored energy function.

This work forms part of a program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

APPENDIX

The following series of vulcanizates were prepared to give rubbers possessing a wide range of degree of crosslinking and initial molecular weight. In each case (except vulcanizates E1-E6) the compounded stock was divided into a number of equal parts and masticated to give different degrees of breakdown. Compounding ingredients and vulcanization conditions were as follows.

Vulcanizates A1-A5

Smoked sheet 100, di-*tert*-butyl peroxide 5 parts by weight. Vulcanization 60 minutes at 140°C.

Vulcanizates B1-B5

Smoked sheet 100, di-*tert*-butyl peroxide 7.5 parts by weight. Vulcanization 60 minutes at 140°C.

Vulcanizates C1-C4

Smoked sheet 100, dicumyl peroxide 2 parts by weight. Vulcanization 90 minutes at 140°C.

Vulcanizates D1-D5

Smoked sheet 100, dicumyl peroxide 3 parts by weight. Vulcanization 60 minutes at 140°C.

Vulcanizates E1-E6

The following amounts of di-*tert*-butyl peroxide were added to 100 parts of masticated smoked sheet. All periods of heating were at 140°C. (1) 2.11 parts (3 hours); (2) 2.02 parts (5 hours); (3) 2.26 parts (1³/₄ hours); (4) 2.20 parts (1¹/₄ hours); (5) 2.18 parts (7 hours); (6) 2.58 parts (7 hours).

Vulcanizates F1-F5

Smoked sheet 100, dicumyl peroxide 3 parts by weight. Vulcanization 60 minutes at 140°C.

Vulcanizates G1-G5

Smoked sheet 100, sulfur 3, zinc oxide 5, stearic acid 1, mercaptobenzothiazole 0.5, phenyl- β -naphthylamine 1 parts by weight. Vulcanization 45 minutes at 140°C.

Vulcanizates H1-H4

Smoked sheet 100, dicumyl peroxide 3 parts by weight. Vulcanization 60 minutes at 140°C.

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Synopsis

Improvement in methods of characterizing the stress-strain properties of vulcanized rubber and of determining its molecular weight prior to vulcanization are described. Experimental results obtained previously by Mullins, Moore, and Watson, in an attempt to relate the physical properties of natural rubber to their network structure, are critically re-examined to take account of these developments. It is shown that if empirical corrections are made for the effect of network flaws due to chain ends and for a second type of network defect equivalent to chain entanglements, then estimates of the degree of crosslinking derived from physical measurements and from chemical determinations are in remarkably close accord.

Résumé

On décrit une amélioration des méthodes de caractérisation des propriétés tension-élongation de caoutchoucs vulcanisés et de détermination du poids moléculaire avant vulcanisation. Les résultats expérimentaux obtenus précédemment par Mullins, Moore et Watson, en vue de relier les propriétés physiques du caoutchouc naturel à leur structure réticulaire, sont réexaminés critiquement afin de tenir compte de ces développements. On montre que si on apporte des corrections empiriques pour l'effet des extrémités relâchées des réseaux et pour un second type de défautuosité réticulaire, correspondant à l'enchevêtrement des chaînes, les estimations du degré de pontage obtenues au départ des mesures physiques et chimiques sont en accord remarquables.

Zusammenfassung

Es wird eine Verbesserung der Methoden zur Charakterisierung des Spannungs-Dehnungsverhaltens von vulkanisiertem Kautschuk und zur Bestimmung seines Molekulargewichts vor der Vulkanisation beschrieben. Exponentielle Ergebnisse, die früher von Mullins, Moore und Watson im Rahmen ihrer Bemühungen die physikalischen Eigenschaften von Naturkautschuk zu seiner Netzwerkstruktur in Beziehung zu bringen, erhalten worden waren, werden im Lichte der hier gegebenen Entwicklungen kritisch überprüft. Es wird gezeigt, dass nach Anbringung von empirischen Korrekturen für die durch Kettenenden verursachten Fehlstellen im Netzwerk sowie für eine zweite, den Kettenverschlingungen äquivalente Art von Fehlstellen, der aus physikalischen Messungen abgeleitete Vernetzungsgrad mit dem auf chemischen Wege bestimmten in bemerkenswert guter Übereinstimmung ist.

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