

Relation between Stress-Strain Behavior and Equilibrium Volume Swelling for Peroxide Vulcanizates of Natural Rubber and *cis*-1,4-Polyisoprene

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Synopsis

Data are reported for the elastic behavior, as described by the parameters C_1 and C_2 , and the equilibrium swelling in *n*-decane, v_r , for dicumyl peroxide vulcanizates of natural rubber and *cis*-1,4-polyisoprene. For natural rubber vulcanizates the correlation between C_1 and v_r can be described in terms of the original Flory-Rehner equation with $\chi = 0.41$. Tentative evidence is presented which favors this equation rather than the later modified form in which the term in $v_r^{1/3}$ is replaced by one in $(v_r^{1/3} - v_r/2)$.

In this note data are presented which define the correlation between the equilibrium volume swelling in *n*-decane of dicumyl peroxide vulcanizate networks of natural rubber and synthetic *cis*-1,4-polyisoprene and their stress-strain behavior in simple extension as interpreted in terms of the Mooney-Rivlin equation,^{1,2}

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

In this equation C_1 and C_2 are constants characterizing the vulcanizate network, and f is the force required to extend the vulcanizate network, initially of cross-sectional area A_0 , to an extension ratio λ . The stress-strain behavior of swollen vulcanizates can be similarly interpreted; C_1 is found to be nearly identical with that observed for the unswollen material, but C_2 is progressively reduced as the degree of swelling is increased. Ultimately for a highly swollen vulcanizate, if measurements can be made under conditions free from interference from finite chain extensibility effects, $C_2 \rightarrow 0$ and,

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

$2C_1$ is therefore to be identified with the constant, G , of the equation derived from statistical theory,³

$$f/A_0 = G(\lambda - \lambda^{-2}) \quad (3)$$

TABLE I
Measurements of C_1 , C_2 , and v_r at 25°C.

[η] dl./g. (toluene)	v_r (<i>n</i> -decane)	C_1 dyne/cm. ² × 10 ⁻⁶	C_2 dyne/cm. ² × 10 ⁻⁶	Sol wt.-%	C_1 (corr.) ^a rubber, dyne/cm. ² × 10 ⁻⁶	Benzene			<i>n</i> -Heptane				
						v_r	χ_B	χ'_B	v_r	χ_H	χ'_H		
2.13	0.0641	0.118	0.563	18.7	0.136	0.314	0.329						
"	0.0947	0.156	0.441	11.3	0.169	0.398	0.411						
"	0.1069	0.242	0.617	9.9	0.259	0.368	0.385						
"	0.1218	0.331	0.637	8.2	0.350	0.366	0.387						
"	0.1401	0.381	0.640	6.5	0.398	0.385	0.406	0.1021	0.416	0.429	0.1470	0.449	0.463
"	0.1562	0.462	0.667	5.1	0.478	0.384	0.406						
"	0.1788	0.534	0.643	3.1	0.544	0.394	0.419						
"	0.1954	0.646	0.725	2.1	0.655	0.418	0.449	0.1426	0.428	0.445	0.2047	0.470	0.489
"	0.2055	0.749	0.760	1.9	0.758	0.414	0.443						
2.12	0.2228	0.922	0.750	1.9	0.933	0.409	0.441						
2.13	0.2408	1.072	0.802			0.416	0.451						
3.02	0.2494	1.110	0.644			0.425	0.460						
2.14	0.2730	1.429	0.794			0.418	0.459	0.1993	0.428	0.453	0.2865	0.486	0.515
2.16	0.2850	1.690	0.899			0.404	0.451						
"	0.3024	1.842	0.880			0.416	0.464						
"	0.3056	1.846	0.864			0.422	0.470						
3.19	0.3147	2.113	0.741			0.408	0.461						
2.22	0.3163	2.076	0.860			0.415	0.467						
"	0.3290	2.310	0.884			0.415	0.470	0.2309	0.420	0.452	0.3300	0.490	0.528
2.20	0.3322	2.356	0.940			0.415	0.471						
"	0.3459	2.706	0.864			0.407	0.468						
"	0.3480	2.734	0.896			0.407	0.469						
"	0.3512	2.672	0.846			0.418	0.480						
"	0.3560	2.894	0.817			0.407	0.472						
3.04	0.3559	2.770	0.880			0.419	0.480						

3.04	0.3559	2.846	0.764	0.412	0.475
—	0.3618	3.220	0.930	0.390	0.460
—	0.3610	3.026	0.784	0.406	0.473
3.00	0.3638	2.862	0.877	0.424	0.486
—	0.3700	3.200	0.761	0.407	0.475
2.73	0.3743	3.318	0.714	0.405	0.475
—	0.3865	3.736	0.634	0.395	0.472
—	0.3965	3.773	0.770	0.411	0.487
3.41	0.1776	0.450	0.900	0.441	
3.41	0.2096	0.647	0.934	0.444	
3.41	0.2448	0.994	1.000	0.417	
3.41	0.2618	1.226	0.964	0.427	
2.92	0.2711	1.330	1.025	0.428	
3.41	0.2752	1.423	0.995	0.424	
2.92	0.2857	1.545	1.068	0.425	
3.41	0.2936	1.645	1.065	0.426	
3.41	0.3091	1.764	1.063	0.437	
3.41	0.3111	1.826	1.026	0.434	
3.41	0.3181	2.169	0.977	0.409	
2.92	0.3258	2.252	1.020	0.414	
2.92	0.3305	2.340	1.045	0.413	
2.92	0.3348	2.479	0.921	0.408	
			1.9	0.454	
			1.3	0.649	
			0.7	0.996	

0.2700 0.409 0.453 0.3808 0.489 0.538

cis-1,4-Polyisoprene
vulcanized with di-
cumyl peroxide at
140–150°C.

* C_1 corrected as detailed in the text for presence of sol rubber.

and is a measure of the degree of physically effective crosslinking. C_2 is clearly a term characterizing departures from this ideal behavior, but its actual physical significance is not apparent at present.

The measurements reported here differ in two respects from similar data for natural rubber published by Mullins.⁴ Firstly, the range of C_1 values has been extended from $0.4 < C_1 < 2.0$ to $0.2 < C_1 < 3.8$ dyne/cm.² $\times 10^6$. Secondly, C_1 has been measured by means of the apparatus and technique described by Greensmith.⁵ Greensmith's technique involves the determination of stress for a predetermined series of λ values, the sample undergoing some measure of stress relaxation, whereas the method used by Mullins⁴ consisted of determining λ for a given stress level and

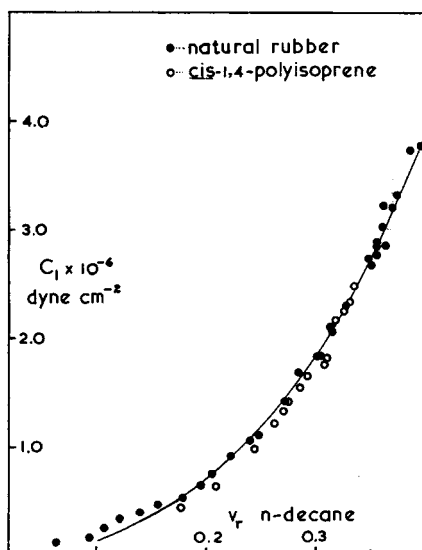


Fig. 1. Relation between the elastic constant C_1 and the equilibrium volume swelling v_r .

involved therefore a certain amount of creep. The present data give further confirmation of the identity of the estimates of C_1 made by these two methods.

Acetone-extracted pale crepe natural rubber and synthetic ca. 92% *cis*-1,4-polyisoprene (Cariflex 305, Shell Chemical Co.) were each mixed on the mill with 1–5 phr of recrystallized dicumyl peroxide and vulcanized as 1 mm. sheets at 140–150°C. The vulcanized sheets were extracted with hot acetone for 24 hr. and dried *in vacuo*; this process removed residual peroxide and peroxide decomposition products but not any rubber remaining unvulcanized (sol rubber). Equilibrium volume swelling in *n*-decane at 25°C., characterized as v_r , the volume fraction of rubber network in the swollen gel, was determined as described previously.⁴ For all but the most lightly crosslinked vulcanizates, the quantity of soluble material extracted during the *n*-decane swelling measurement was negligible, and hence the

v_r values estimated referred to a vulcanizate network which had received a comparable extraction treatment and undergone therefore a similar extent of supercoiling to that used for the C_1 determination. For the few very lightly vulcanized materials, from which an appreciable amount of sol rubber was extracted during swelling in *n*-decane, this conclusion as regards supercoiling is no longer valid. A correction was applied therefore to the cross-sectional area of the vulcanizate used in the C_1 determination, C_1 being increased by the factor $[100/(100 - \text{volume-\% sol rubber})]^{2/3}$. This correction, which is the same as that used by Mullins,⁴ will be discussed in detail elsewhere.⁶

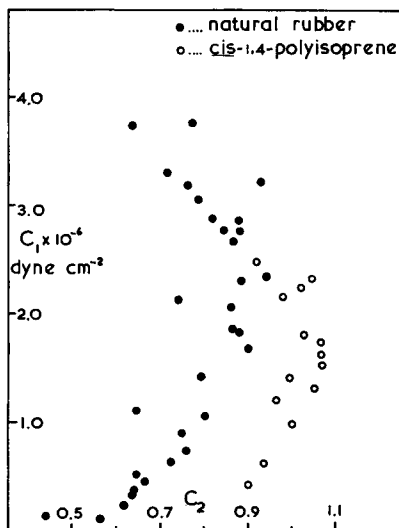


Fig. 2. Relation between the constants C_1 and C_2 . (C_1 and C_2 are expressed in the same units.)

C_1 , C_2 , and v_r data are given in Table I. The plot of C_1 versus v_r (Fig. 1) is, for natural rubber, identical over the relevant C_1 range with that observed by Mullins.⁴ *cis*-1,4-Polyisoprene vulcanizates seem to conform to a slightly different C_1 - v_r relation to that found for natural rubber. In Figure 2 the parameter C_2 is plotted as a function of C_1 ; within the rather large scatter, C_2 appears to be a smooth function of C_1 with a maximum at $C_1 = \text{ca. } 2.0$. Slightly higher C_2 values are observed for *cis*-1,4-polyisoprene.

The theoretical relation between C_1 and v_r in the form originally proposed by Flory⁷ is,

$$-\ln(1 - v_r) - v_r - \chi_D v_r^2 = (2V_0 C_1 / RT) v_r^{1/2} \quad (4)$$

where V_0 is the molar volume of the solvent (*n*-decane) and χ_D the solvent-polymer interaction parameter. Values of χ_D obtained by application of

this equation are included in Table I. A value of $\chi_D = \text{ca. } 0.41$ is indicated over most of the v_r range. For data for which $v_r > 0.18$ the arithmetic mean value of χ_D is 0.411 (standard deviation 0.008) and the line in Figure 1 is drawn for this value.

χ_D for *cis*-1,4-polyisoprene vulcanizate networks is slightly larger than for natural rubber networks, especially at low v_r values, though such a difference is not observed⁸ in the osmotic behavior of the two rubbers in dilute solution ($v_r < 0.015$) in toluene. While this difference in χ_D may be real, it could be an artifact arising in the estimation of C_1 from the plots of $f[2A_0(\lambda - \lambda^{-2})]^{-1}$ versus λ^{-1} . In general these plots are of rather different shape for each of the two polymers; for a given C_1 value, the deviation from linearity occasioned by the incidence of finite chain extensibility effects occurs at rather greater λ values for vulcanizates of *cis*-1,4-polyisoprene than for those of natural rubber and further, C_2 values are somewhat larger for the former material. Since C_1 values are determined by extrapolation of the linear portions of these plots, relatively slight differences in the procedure adopted for this extrapolation between vulcanizates of natural rubber and *cis*-1,4-polyisoprene could readily account for small systematic differences in the values of C_1 estimated for the two polymers.

Application of the modified Flory equation,⁹

$$-\ln(1 - v_r) - v_r - \chi'_{D'}v_r^2 = (2V_0C_1/RT)(v_r^{1/3} - v_r/2) \quad (5)$$

gives values of $\chi'_{D'}$ (Table I) which are greater than χ_D and show a greater dependence on v_r . Inasmuch as there is no independent evidence as to the value of the interaction parameter for the natural rubber-*n*-decane system, or its concentration dependence in this particular v_r range, these data in no way constitute an experimental test of the relative merits of eqs. (4) and (5).

For some of the vulcanizate networks, values of v_r in benzene have been estimated, and χ_B and $\chi'_{B'}$ calculated (Table I). For this solvent the extensive work of Gee and his collaborators¹⁰ has provided values of the solvent interaction parameter of 0.40–0.42 for $0.1 < v_r < 0.9$. While these values apply only to unvulcanized natural rubber, the crosslinking of rubber chains without any modification or incorporation of foreign atoms would not be expected to induce any significant change in the value of χ , a conclusion for which theoretical evidence has been adduced.¹¹ The vulcanization of natural rubber by dicumyl peroxide is believed to be such an uncomplicated crosslinking process,^{12,13} but the possible introduction of some cyclized units into the main chain cannot be entirely discounted. Gee's¹⁰ value of 0.40–0.42 is in closer accord with the values estimated for χ_B from eq. (4) than those of $\chi'_{B'}$ deduced from eq. (5) and to this extent these present data may be said to favor eq. (4).

The data for *n*-heptane (Table I) also provide evidence from which the same conclusion can be drawn. In this case the value of $\chi'_{H'}$ is markedly dependent on v_r and for $v_r > \text{ca. } 0.17$, $\chi'_{H'} > 0.50$. If these values are also applicable to the unvulcanized rubber then, dependent on the molecular

weight, partial miscibility of natural rubber and *n*-heptane should be observed above a critical value of v_r , the critical conditions being:¹⁴

$$\chi_{\text{crit.}} = 0.5 + (M/68)^{-1/2} \quad (6)$$

$$v_{\text{crit.}} = (M/68)^{-1/2} \quad (7)$$

where M is the molecular weight of the rubber.

Partial miscibility is not observed with *n*-heptane, and hence either the values of χ'_H are not applicable to the unvulcanized state or the values of χ_H from eq. (4) are to be preferred.

The above arguments in favor of the original form of the Flory equation [eq. (4)] in preference to the later modified form [eq. (5)] are clearly only valid insofar as the precision of C_1 as a measure of the degree of physically effective crosslinking is considerably greater than the difference between the $v_r^{1/2}$ and $(v_r^{1/2} - v_r/2)$ terms in eqs. (4) and (5). While the significance of C_1 measurements on unswollen vulcanizates (such as are reported here) might be said to be obscured by the existence of a comparable C_2 value, the close parity (ca. 5%) which exists in favorable cases between C_1 values obtained for unswollen vulcanizates and those for the same vulcanizates when highly swollen when $C_2 \rightarrow 0$ supports the contention that C_1 as measured here is in fact a sufficiently precise measure of physically effective crosslinking.

In conclusion it must be admitted that despite the above evidence adduced in support of the original form of the Flory equation [eq. (4)] in preference to the later modified form [eq. (5)], these equations are based on theoretical treatments which are not entirely satisfactory and both may well be incorrect to an extent greater than the difference between the terms $v_r^{1/2}$ and $(v_r^{1/2} - v_r/2)$ would imply, since this difference amounts to only some 20% for $v_r = 0.2-0.3$.

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Résumé

On décrit le comportement élastique au moyen des paramètres C_1 et C_2 , et l'équilibre de gonflement dans le n -décane, v_r , pour le caoutchouc naturel et le *cis*-1,4-polyisoprène vulcanisés au peroxyde de dicumyle. Pour le caoutchouc naturel vulcanisé, la corrélation entre C_1 et v_r peut être décrite au moyen de l'équation de Flory-Rehner, avec $\chi = 0.41$. On démontre que cette équation est plus favorable que la forme modifiée ultérieurement dans laquelle le terme en $v_r^{1/2}$ est remplacé par un autre en $(v_r^{1/2} - v_r/2)$.

Zusammenfassung

Ergebnisse für das elastische, durch die Parameter C_1 und C_2 beschriebene Verhalten und die Gleichgewichtsquellung in n -Dekan, v_r , von Dicumylperoxydvulkanisaten von Naturkautschuk und *cis*-1,4-Polyisopren werden mitgeteilt. Bei Naturkautschukvulkanisaten kann die Beziehung zwischen C_1 und v_r durch die ursprüngliche Flory-Rehner-Gleichung mit $\chi = 0,41$ wiedergegeben werden. Vorläufige Ergebnisse lassen erkennen, dass diese Gleichung besser zutrifft als die später modifizierte Form, bei welcher der Term mit $v_r^{1/2}$ durch einen mit $(v_r^{1/2} - v_r/2)$ ersetzt wird.

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