Correlations involving the Mooney–Rivlin C_2 constant and the number of chain atoms between physical entanglements, N_c

Raymond F. Boyer and Robert L. Miller
Michigan Molecular Institute, Midland, Michigan 48640, USA

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We start with two previously calculated semi-empirical equations: (1) $C_2/C_1 = K_1A^{-2}$ (for $2C_1 = 0.2$ MPa). K_1 is a constant and A is the area per polymer chain; (2) $N_c = K_2A^{0.67}$ where K_2 is another constant. It follows from these two relationships that: C_2/C_1 (at $2C_1 = 0.2$) $= K_3N_c^{-3}$. N_c, determined for bulk polymers, increases on dilution with a solvent according to $N_c(\phi_2) = N_c(\phi_2 = 1)\phi_2^{-r}$ where ϕ_2 is the volume fraction of elastomer and r is a constant for a given elastomer, usually unity. For vulcanizates prepared in the presence of diluents but tested in the bulk state, one predicts $C_2/C_1 = K_4\phi_2^{3r}$ if entanglements are the sole source of the C_2 term. Plots of log C_2/C_1 against log ϕ_2 show slopes ranging from 0.5 to 3.0 but more commonly near unity. There is wide discrepancy between different authors. We conclude that chain entanglement cannot be the sole source of the C_2 term but that several factors probably operate. Different theories and ideas about the origin of the C_2 term are briefly reviewed. Excellent linear plots of log C_2/C_1 against log $2C_1$ are presented for *trans*-polypentenamer and for Hevea rubber. In general, sufficient data for the rigorous testing of the $C_2/C_1 - \phi_2^{3r}$ relationship are not available. A correlation of f_e/f with area per chain (where f_e is the energetic contribution to the total force, f) increases rapidly at small areas but levels off above ~0.4 nm^2. All studies reported herein are based on published data.

(Keywords: elastomers; networks; entanglements; stress–strain; *trans*-polypentenamer; Hevea; energetic force; entropic force)

(1) INTRODUCTION

It has been known since the early studies of Treloar[1] and Gee[2] that real elastomers do not follow the theory of rubber elasticity, even when tested under near equilibrium conditions. This departure from theory is most commonly expressed by the Mooney–Rivlin equation[3–5]

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

where f is the force of retraction at extension ratio $\lambda = l/l_0$, and C_1 and C_2 are the Mooney–Rivlin constants. Problems associated with the use and interpretation of this equation have been stressed by Treloar[5,6]. Mark has presented an extensive literature review of factors affecting C_1 and C_2[7]. Equation (1) holds only under rather restrictive conditions (and is not a so-called constitutive equation[8]) to describe the behaviour of elastomers over a wide range of experimental conditions. In our previous work[9,10], to be discussed shortly, we followed two suggestions by Treloar[11]:

(1) Use of values of C_1 and C_2 obtained in simple tension at extension ratios lying between 1.2 and 2.0.

(2) Comparison of the dependence of C_2 on chemical structure for a variety of elastomers should be made at a fixed $2C_1$. This commonly requires the preparation of log–log plots of C_2/C_1 against $2C_1$ (such plots are usually linear or slightly curved) from which values of C_2/C_1 at a pre-selected $2C_1$ can be read.

For undiluted rubbers, we found[9,10] an empirical relationship between C_2/C_1 (at constant $2C_1$) and cross-sectional area per polymer chain A:

$$C_2/C_1 \text{ (at constant } 2C_1) = K_1A^{-m} \qquad (2)$$

where the exact value of m depends on the value of $2C_1$ selected: m is 1.58 for $2C_1 = 0.1$ MPa and is 2.01 for $2C_1 = 0.2$ MPa. Equation (2) might imply a dependence of C_2/C_1 on intermolecular forces and/or intermolecular packing. In a parallel study[12,13], it was shown that the number of chain atoms N_c between points of physical entanglement (in undiluted rubbers) varies with area per chain as

$$N_c = K_2A^n \qquad (3)$$

Note: All earlier studies[9,10,12,13] were based on literature values of C_1, C_2 and N_c, as is also true for the present study. The earlier study[12] placed n at ~0.5 while a more detailed examination using more data points placed n at 2/3[13].

We have shown elsewhere[14] that A increases as M_0/Z_0 where M_0 is the mass of a monomer unit and Z_0 is the number of chain atoms per monomer unit. This is equivalent to stating that A, and hence N_c through equation (3), increases with the mass and bulkiness of a substituent on the polymer chain. Such a prediction for N_c was first tested and verified by Porter and Johnson[15] for a limited number (four) of polymers.

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Table 1 Values of C_2/C_1 and N_c for several elastomers

Elastomer	A^a (nm^2)	C_2/C_1 at $2C_1=0.2^a$	$N_c^{b,c}$
Polyethylene	0.183	4.4	270
t-Polypentenamer	0.181	2.88	270^d
cis-Polybutadiene	0.207	1.90	300
cis-Polyisoprene	0.280	0.766^{e,f}	8.24^{g,h}
Butyl rubber ≈ PIB	0.41	1.50^i	540
		0.64	540
		0.36	540
Poly(dimethylsiloxane)	0.436	0.58	630
Poly(ethylacrylate)	0.9	0.12	830^j

[a] From Table I of ref. 10 except where noted. Cross-sectonal area per polymer chain, $1\ \mathrm{nm}^2 = 10\ \text{Å}^2$ units

[b] From Table II of ref. 13

[c] N_c is number of chain atoms between entanglements

[d] Assumed to be same as for PE

[e] *Hevea Brasiliensis* or NR

[f] Calculated from parameters in *Table 5*

[g] Synthetic *cis*-PI

[h] Table IV of ref. 13

[i] See discussion p. 807, ref. 10. Values of $2C_1$ are 0.124, 0.146 and $0.138\ \mathrm{N\,mm^{-2}}$ respectively from top to bottom

[j] Estimated from techniques given in ref. 13

Note: We express all values of $2C_1$ and $2C_2$ in Megapascals, MPa, the international unit. Many of our sources give $\mathrm{N\,mm^{-2}}$ or $\mathrm{kg\,cm^{-2}}$. $1\ \mathrm{MPa} = 1\ \mathrm{N\,mm^{-2}} = 10.2\ \mathrm{kg\,cm^{-2}}$

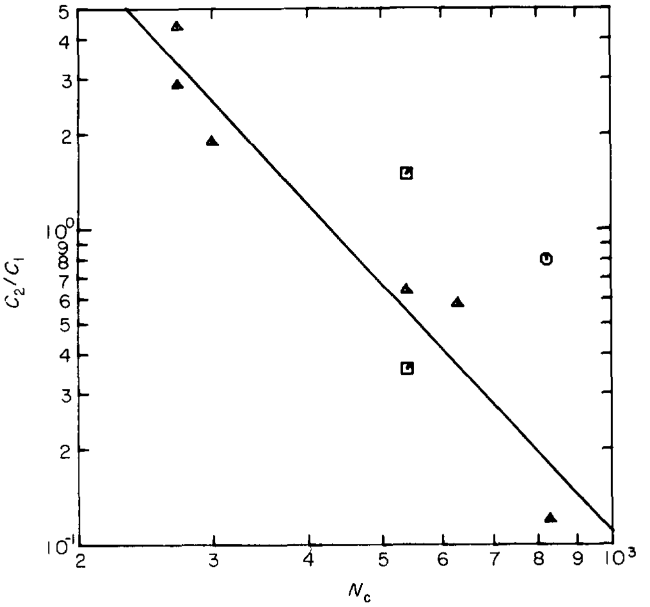

Figure 1 Correlation of C_2/C_1 (at $2C_1 = 0.2$ MPa) with N_c values from *Table 1*. Extreme values for PIB, □, and for *cis*-PI, ○, were not used for regression analysis. The line fitted to the remaining data points has the equation: $\log C_2/C_1\ (2C_1 = 0.2\ \mathrm{MPa}) = 6.881 - 2.613 \log N_c$

Elimination of A from equations (2) and (3) leads at once to the equation

$$(C_2/C_1) = K_3 N_c^{-m/n} \text{ (at constant } 2C_1) \qquad (4)$$

For $2C_1 = 0.2$ MPa, $m/n \sim 3$. (**Note:** Since equations (2) and (3) are for undiluted elastomers, the same must be true for equation (4).) The available data are plotted in *Figure 1* according to equation (4). There is considerable scatter. Natural rubber (NR) is evidently a deviant system because its value of N_c is twice that expected from the trend line represented by equation (3)[13], whereas it lies reasonably well on the trend line for equation (2)[10] (see also *Table 1*). *Figure 1* shows a slope of −2.61 instead of −3.

In what follows, we assume that equation (4) holds also in the presence of diluent. It does require modification, however. This arises from the fact, first reported by Price *et al.*[16] and subsequently verified for NR and other polymers (see Table III of ref. 7), that vulcanization of NR in the presence of a diluent leads to a sharp drop in C_2 for the diluent-free bulk vulcanizate. A physically entangled bulk net work characterized by N_c (bulk) will have a larger effective entanglement distance on dilution. Following Graessley[17], we may write

$$N_c(\phi_2) = N_c(\phi_2 = 1)/\phi_2^r \qquad (5)$$

where ϕ_2 is the volume fraction of elastomer and r is a constant. Substitution of this equation into equation (4) leads to

$$C_2/C_1 \text{ (at constant } 2C_1) \approx K_4 \phi_2^{3r} \qquad (6)$$

for a given elastomer. Equation (6) predicts a very sharp drop in C_2/C_1 as diluent is used during crosslinking, especially for $r > 1$. A numerical test of this equation will be discussed later.

There is disagreement in the literature about the value of r in equations (5) and (6). Porter and Johnson[18] present a summary of the older literature while a more recent account is that given by Graessley[17]. Onogi *et al.*[19] find $r = 2.0$ for heterodisperse polystyrenes whereas Graessley *et al.*[20a] as well as Gupta and Forsman[20b] find $r = 1$ for anionic polystyrene. This suggests that polymer heterogeneity may affect values of r. Solvent probably also plays a role. Fetters[21] has made a study of the viscosities of anionic synthetic *cis*-polyisoprenes in decane as a function of molecular weight. He finds $r = 1$. In general we shall assume $r = 1$ for elastomers to be discussed in Section 3.

Equation (4) is designed to compare a series of elastomers as was done in *Figure 1*. Equation (5) is polymer specific since $N_c(\phi_2 = 1)$ is characteristic of a given elastomer. That same elastomer has a definite value of C_2/C_1 at a given $2C_1$. We assume that substitution of equation (5) in equation (4) gives a polymer specific relationship expressed in a simple form in equation (6) but having the more general form:

$$C_2/C_1 = K_4 \phi_2^{r\,m/n} \qquad (6a)$$

r may be polymer specific[17–20] although it is most likely unity; n has the empirical value of 2/3[13]. Thus,

$$C_2/C_1 = K_4 \phi_2^{1.5m} \qquad (6b)$$

m is a function of $2C_1$, having values of ~1.6 at $2C_1 = 0.1$ MPa and ~2 at 0.2 MPa[10]. We have made a plot of C_2/C_1 against A at $2C_1 = 0.05$ MPa. The scatter is considerable but it does appear that $1 < m < 1.5$. As stated earlier, equation (6) applies only to $2C_1 = 0.2$ MPa. Vulcanization in a diluent frequently leads to lowered values of $2C_1$, even down to 0.05 MPa (Table III of ref. 7). The slope in equation (6b) might well need to be adjusted in some cases for actual values of $2C_1$.

Finally, we note that the constant, K_4 in equation (6) contains the polymer specific parameter $N_c^{-m/n}(\phi_2 = 1)$.

No attempt has been made to test this out, largely through lack of adequate data.

(2) THEORIES OF THE MOONEY–RIVLIN EFFECT

A major purpose of this paper is to inquire whether the C_2 term depends on intermolecular forces as equation (2) implies or on N_c as equation (4) suggests, or on a combination of both factors. We indicated earlier (pages 807–809 of ref. 10) that there are proponents for both points of view. Before this question may be addressed, some theoretical considerations about C_2 must be introduced. A complete theory of rubber elasticity should explain at least five facets of the behaviour of real elastomers:

(1) Stress deviations as measured by $2C_2$ and/or C_2/C_1 in equation (1);

(2) C_2/C_1 decreases on addition of diluent to a network formed in the bulk state;

(3) C_2/C_1 generally decreases for networks formed in the presence of diluent and tested in the dry bulk state (addition of diluent to the bulk vulcanizate further depresses C_2);

(4) the exceptions to point 3, which will be discussed later; and

(5) extraction of a network to remove non-network material may reduce C_2/C_1 even when tested in the bulk state.

Examples and/or references for points 1–4 are found in ref. 7. Point 5 is treated in Appendix 2 of ref. 10.

At least five theoretical attempts have been made to relate C_2/C_1 to molecular parameters of an elastomer network. In the order of the first publication in each series, these are:

(i) Meissner and his colleagues[22–25] have indicated from network theory and shown by experiment that C_2 depends on chain entanglements, being highest when N_c (our notation) is smallest. This series of papers covers points 1–3. Meissner and Klier[25] predicted and found a high value of C_2 for *trans*-polypentenamer (*t*-PPE) on the basis that absence of side groups would lead to a small value of N_c. This conclusion about N_c is consistent with both the findings of Porter and Johnson[15] and with our results stated in the form of equation (3). *t*-PPE does indeed have a very small cross-sectional area, 0.181 nm^2, and compares closely with 0.183 nm^2 for polyethylene (PE) (see *Table 1*).

(ii) Schwarz, in several theoretical papers[26–28], explains C_2 as arising from an alignment or local ordering of polymeric material (network, chain ends and non-network material) on application of stress. He states that his theory provides an interpretation for the observations indicated above by points 1–3 inclusive. We have suggested that it also provides an explanation of point 5 (see Appendix 2 of ref. 10). Schwarz emphasizes[28] that his view of local ordering does not embrace the bundle theory. Gee had earlier[2] proposed local order as the origin of C_2.

(iii) Ronca and Allegra[29] present a theoretical treatment of a real polymer network in contrast to the phantom networks which were used in earlier theories of rubber elasticity. The abstract in their paper states: 'The intermediate model can explain, at least to some extent, the so-called Mooney effect'.

(iv) Edwards[30] has also made a similar contribution.

(v) Flory[31] likewise offers a theoretical treatment of a real network. In his concluding remarks, he cautions that he has used intuitive inputs which may involve appreciable error so that precise conformity with experiment should not necessarily be expected. He further states that his theory is commensurate with experimental values of C_2/C_1 tending to fall in the range of 0 to 1, based on Mark's tabulations[7].

Several comments are in order concerning the latter theories[29–31].

(1) Gumbrell, Mullins and Rivlin[32] were the first to propose that the $2C_2$ term arises from finite dimensions of the rubber chains. Real chains restrict the number of available conformations.

(2) It follows from equation (2) that C_2/C_1 $(2C_1 \sim 0.2) \simeq K_1/A^2$ and hence $C_2/C_1 \simeq KN^2$ where N is the number of real chains per m^2. This might seem to confirm the phantom chain concept. At the same time the number of physical entanglements is greater the larger is C_2/C_1.

(3) It is not clear to us if Flory's specific theory[31] covers the higher C_2/C_1 ratios of 3 to 5 which are found for polymers of small cross-sectional area such as PE, polybutadiene (PBD), and *t*-PPE[10]. Schwartz, who has studied this question in some detail, is convinced that the Flory treatment can predict a top limit of C_2/C_1 no greater than unity[27].

Thus, current theories appear correct in principle but wanting in specifics. We suggest that while the introduction into the theories of real chains of undefined nature (rather than phantom chains) marks a major advance, it will ultimately be necessary to consider the characteristics of specific polymer chains. Our studies with area per chain (one such characteristic parameter) address the issue of the variance in physical structure and properties of real polymer chains.

With this as background, we may now discuss points 2–5 above.

(3) THE ROLE OF DILUENTS IN ELUCIDATING THE ORIGIN OF THE C_2 TERM

Diluents may affect both $2C_1$ and $2C_2$ in any of three ways, as already indicated in Section 2.

(A) Addition of a diluent to a vulcanizate crosslinked in the bulk state reduces $2C_2$; frequently to zero when ϕ_2 is below about 0.20.

(B) Vulcanization with diluent followed by evaporation of the diluent or by extraction with a solvent (which also removes sol) lowers $2C_2$ for the dried vulcanizate relative to vulcanizate crosslinked in bulk state, in some cases to zero.

(C) Dilution of the dry vulcanizate of B above may lead to a further reduction of $2C_2$ depending on dilution during vulcanization.

So if (A) is true, (C) may follow. These facts should permit one to draw conclusions about the factors which control $2C_2$. However, this desideratum is not too well realized in practice, due, in part, to a paucity of appropriate data. We shall cover only points (A) and (B) below, as being most relevant to subsequent discussion. Moreover, if (A) is true, (C) should follow.

A vulcanizate prepared in the bulk state can be tested in the diluted swollen state after swelling with a good

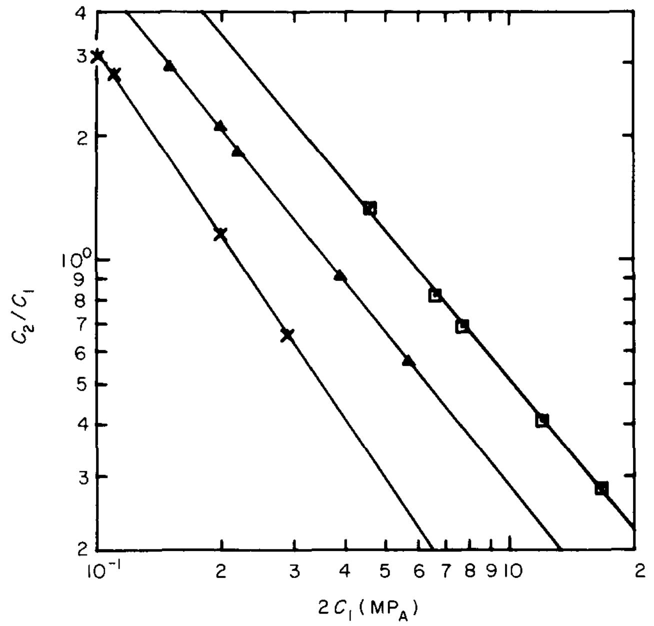

Figure 2 C_2/C_1–$2C_1$ plot for *trans*-polypentenamer (*t*-PPE) at three values of ϕ_2, the volume fraction of elastomer present in paraffin oil during vulcanization. $\phi_2=0.96$, □; $\phi_2=0.47$, △; $\phi_2=0.31$, ×. C_1 and C_2 were measured on the benzene extracted, dried vulcanizates. Data of Meissner and Klier[25]

solvent. C_2 usually decreases linearly and may become zero with $\phi_2 \leq 0.2$.

Gee[2,3] presented the original argument that C_2 had its origin in intermolecular forces since addition of diluent, which lowers C_2, would certainly decrease intermolecular forces between polymer chains. This point of view is supported by Schwarz[26].

Dusek and Prins[33] suggested that increased swelling should cause entanglement points to act more and more like permanent crosslinks so that C_2 should decrease. However, they then expected that C_1 should also increase. Instead, C_1 is relatively constant (see Table V of ref. 7) or, as they note, may actually decrease. Thus, they argue against the role of physical entanglements and clearly favour the local order concept. It is not clear to us how much sol matter is extracted during this swelling step, especially at higher degrees of swelling. The resulting lowering of $2C_2$ could arise either from the fact that the polymer is swollen or extracted, or both. Mark (page 502 of ref. 7) points out that under swelling conditions, the quantity $2C_2\phi_2^{-4/3}$ is postulated to be constant. According to Mark's extensive tabulation (Table V of ref. 7), this is certainly not the case. The departure from any semblance of constancy increases as ϕ_2 decreases, suggesting possibly that leaching of sol may play a role in addition to pure dilution effect. We mention this leaching effect as a precautionary factor without asserting that this is so.

Schwarz[26] suggested that vulcanization in solution gives rise to supercoils which collapse on removal of the solvent. On subsequent elongation, there is no, or a greatly reduced, opportunity for a local ordering of chain segments. Moreover, the sol fraction which participates in this ordering has generally been removed by extraction (see later discussion).

The physical entanglement concept likewise can explain the decrease in C_2 as indicated by equation (6), introduced above. This equation permits, in principle, a numerical test to be made. In actual practice, there are two difficulties.

First, $2C_1$ is frequently decreased, or at least changed, for vulcanizates prepared in the diluted state (see Table III of ref. 7). Hence, it is generally impossible to make a comparison of C_2/C_1 at constant $2C_1$ as a function of ϕ_2. *t*-PPE is the only example which we have found where sufficient information exists. This system will be discussed in detail later.

Secondly, some polymers, such as ethylene–propylene elastomers and *t*-PPE, are exceptions to the finding that vulcanization at $\phi_2<1$ sends C_2 to zero. For example, Kirkham[34] prepared vulcanizates of ethylene–propylene–diene terpolymer (Nordel® 1070) with 0 to 51.5% diluent present. These vulcanizates were extracted and tested in the bulk state. It was apparent that C_2 would not reach zero even at very high levels of diluent during crosslinking.

Meissner and Klier[25] vulcanized 3 sets of *t*-PPE in paraffin oil with dicumyl peroxide at $\phi_2=0.96$, 0.74 and 0.31. The benzene-extracted networks were tested in the bulk state at various levels of crosslink density. They also measured $2C_1$ and $2C_2$ for the non-extracted networks. *Figure 2* is a plot of C_2/C_1 values against $2C_1$ for these three levels of dilution during vulcanization but in the dry state after extraction. These plots are linear and essentially parallel (see *Table 2*). The plot for $\phi_2=0.96$ lacks the curvature reported by us earlier (Figure 5 of ref. 10), which data were in a written communication from Dr Meissner. The present results are from the final publication[25]. If one accepts a linear extrapolation to lower and to higher values of $2C_1$ than those measured, values of C_2/C_1 can be estimated at three arbitrary values of $2C_1$, for example, namely at 0.20, 0.35 and 0.60 MPa.

A plot of C_2/C_1 vs. ϕ_2 at these three arbitrary values of $2C_1$ is shown in *Figure 3*. The individual curves appear to be concave downward although they have been fitted with a linear regression whose parameters are given in *Table 3*. It is clear that C_2/C_1 increases approximately with the first power of ϕ_2 and certainly not with ϕ_2^3 as equation (6) predicts with $r=1$. In the absence of a catastrophic slope change, a C_2/C_1 of zero does not seem likely at $\phi_2>0.1$.

In the discussion above related to equation (6b) we mentioned that the slopes of lines fitting data plotted as in *Figure 3* might well be a function of the value of $2C_1$. This does seem to hold true for the data in *Figure 3* as seen by visual inspection or numerically in *Table 3*. We have not located data on other elastomers which would permit preparation of plots such as those in *Figures 2* and *3*. Consequently, our analysis procedure for elastomers

Table 2 Parameters of straight lines in *Figure 2* for *trans*-polypentenamer [$\log C_2/C_1=\alpha+\beta\log(2C_1)$]

ϕ_2[a]	α	β	R^2[b]	SE[c]
0.96	−0.292	−1.20	0.99865	0.0112
0.47	−0.547	−1.23	0.99977	0.0050
0.31	−0.974	−1.48	0.99930	0.0105

[a] Volume fraction of polymer present during vulcanization in paraffin oil. The $\phi_2=0.96$ was measured as is; the other two were extracted and dried prior to testing
[b] Coefficient of regression
[c] Standard error in $\log(C_2/C_1)$
Note: Units of $2C_2$ and $2C_1$ are MPa

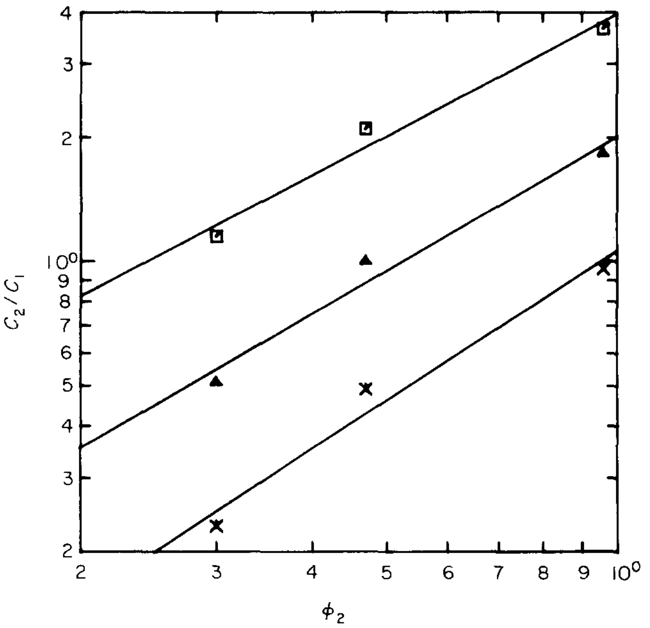

Figure 3 C_2/C_1–ϕ_2 plot to test equation (6) at three values of $2C_1$: $2C_1 = 0.2$ MPa, □; 0.35 MPa, △; 0.60 MPa, ×. Values of C_2/C_1 were estimated from the *Figure 2* plots for *t*-PPE

Table 3 Parameters of straight lines in *Figure 3* [$\log C_2/C_1 = \alpha + \beta \log \phi_2{}^a$]

$2C_1$ (MPa)	α	β	$R^{2\,b}$	SE^b
0.20	0.597	0.973	0.976	0.055
0.35	0.301	1.108	0.974	0.063
0.60	0.0261	1.202	0.973	0.072

[a] Volume fraction of polymer present during vulcanization in paraffin oil. Values of $2C_1$ and $2C_2$ were determined on extracted vulcanizate
[b] See footnotes *b* and *c* of *Table 2*

must be illustrated by the schematic 'data' of *Figure 4*. Real data on Mooney–Rivlin constants as found in the literature are obtained under any of four conditions.

(1) Vulcanization in the bulk, no extraction of solubles (line A–B).

(2) Vulcanization in the bulk followed by extraction with a solvent which removes sol (line C–D).

(3) Vulcanization in a diluted state followed by solvent extraction of the diluent which removes the sol fraction. The extractant is then removed by drying (diamonds in *Figure 4*).

(4) More rarely, the diluent is removed after vulcanization by vacuum drying, which leaves the sol in the vulcanizate.

Vulcanizates prepared in the presence of diluent tend to exhibit decreased values of $2C_1$ because of reduced efficiency of crosslinking. This effect is illustrated by the *t*-PPE data of *Figure 2*. This tendency can be offset by using more drastic vulcanization conditions, which is not often done in practice.

In *Figure 4*, a vertical cut through any of the 'data' points (diamonds) intersects lines A–B and C–D yielding values of C_2/C_1 at a fixed $2C_1$, as indicated for the point $\phi_2 = 0.2$. If this vulcanizate, $\phi_2 = 0.2$, has indeed been extracted, it should be compared with line C–D. In the absence of data leading to construction of line C–D, the comparison must use line A–B, even though this gives incorrect results. One then prepares a plot of C_2/C_1 values thus obtained at constant $2C_1$ against ϕ_2. This plot has only two points on it. A family of lines is obtained at different values of $2C_1$.

This procedure is illustrated in the top three lines of *Figure 5* for *cis*-PBD vulcanizates prepared in diluent and leached with benzene, using the Mooney–Rivlin data of Ong and Stein[35]. In this instance, line C–D type data were available from the work of other authors, as collected in Figure 8 of ref. 10. Evidently, one cannot place much

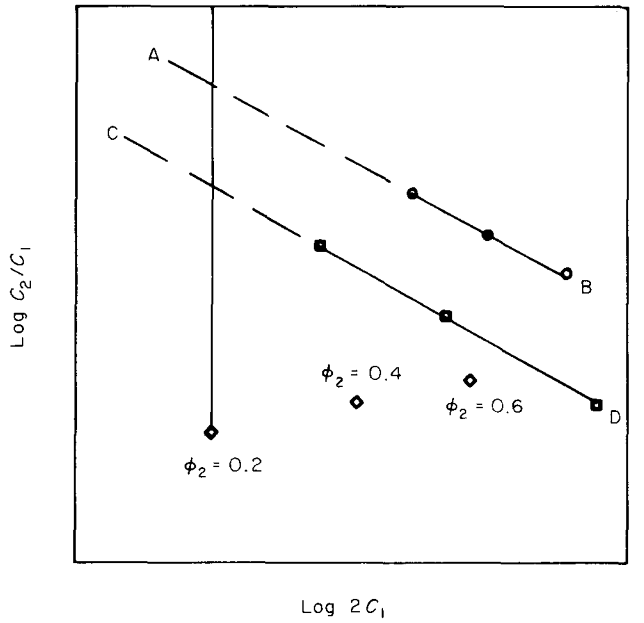

Figure 4 Schematic C_2/C_1–C_1 plot for estimating values of C_2/C_1 at $\phi_2 = 1$ when such measurements are not given by the authors studying vulcanization in solution. Line A–B is based on real data at $\phi_2 = 1$, vulcanizate not extracted; C–D the same but vulcanizate extracted and dried. ◇ signifies vulcanization at indicated ϕ_2 followed by extraction and drying

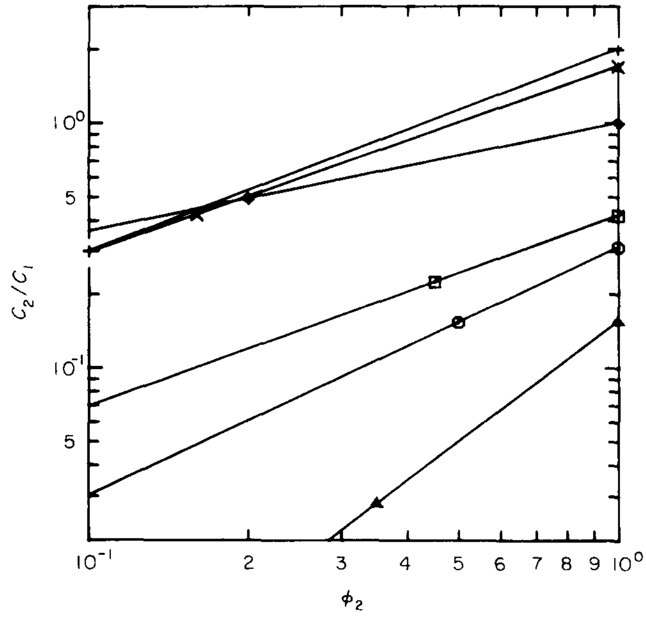

Figure 5 C_2/C_1–ϕ_2 plots for *cis*-PBD's vulcanized in the diluted state, extracted and dried. Top three lines, data of Ong and Stein[35]: $2C_1 = 0.100$ MPa, +; 0.117 MPa, ×; 0.195 MPa, ◇. Bottom three lines data of de Candia *et al.*[36]: $2C_1 = 0.047$ MPa, □; 0.064, ○; 0.126, △. Bottom set of C_2/C_1 values should be multiplied by 10

Table 4 Approximate slopes of log (C_2/C_1) vs. log ϕ_2 lines for natural rubber

Diluent[a]	$2C_1$ (MPa)	Approximate slope[b]	Ref.
Decalin	0.070	1	16
	0.10	2	16
	0.137	2	16
n-Decane	0.119	3	16
Decalin	0.115	1.8	37
	0.122	2.0	37
	0.181	2.0	37

[a] Diluent was used during vulcanization. A benzene extraction removed the diluent and sol fraction. The vulcanizates were tested in the dry state

[b] Estimated from the log–log plots of C_2/C_1 vs. ϕ_2 with two points per line, by comparison with slopes of construction lines having slopes of 1, 2 and 3

credence in the slope of a line with only two data points; and nothing can be deduced about curvature. Considering the three lines in total, one can conclude that the slope is unity or less, more or less in agreement with the *t*-PPE data of *Figure 3*. The Ong and Stein data do not indicate a $C_2 \rightarrow 0$ even at $\phi_2 = 0.1$.

In complete contrast with the work of Ong and Stein is that of de Candia, Amelino and Price[36] who do not cite their source of *cis*-PBD but do experiments apparently identical with those of Ong and Stein. This data is represented by the bottom three lines of *Figure 5*. For this data, the slope increases from unity to 2 as $2C_1$ increases from 0.047 to 0.126. Moreover, C_2 is zero for ϕ_2 of 0.30 and 0.25. Note that actual values of C_2/C_1 have been divided by 10 to allow comparison on the same graph with Ong and Stein data.

One obvious difference in the two sets of lines in *Figure 5* is that $2C_1$ ranged from 0.047 to 0.126 MPa in the de Candia *et al.* data but from 0.10 to 0.195 in that of Ong and Stein. However, other possible differences, as in $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_w/\bar{M}_n$, and exact procedural details, could be quite substantial.

Discrepancies of this same type have been noted for NR. This data is collected in *Table 4* where it is seen that the slopes range from ~1 to ~3 and depend on the type of diluent present during vulcanization. These authors did not give values of C_2/C_1 for $\phi = 1$ at different values of $2C_1$. Hence, we had to estimate them from selected sets of data on NR. The results are shown in *Figure 6* and discussed in Appendix I, which does not refer to benzene extracted vulcanizates. Assuming that the data points of Allen *et al.*[41] in *Figure 6*, lying below the line, refer to benzene extracted vulcanizates, one would estimate slightly lower values of C_2/C_1 at $\phi_2 = 1$, but this would not appreciably reduce the slopes given in *Table 4*.

Finally, we note data of Johnson and Mark[42] for poly(dimethylsiloxane) (PDMS) vulcanized in cyclohexane, extracted with benzene and dried. The range of $2C_1$ values increases from 0.036 to 0.059 as ϕ_2 drops from 1.0 to 0.30. The log–log plot of C_2/C_1 vs. ϕ_2 assuming constant $2C_1$ has a slope of unity. If corrections to C_2/C_1 for actual $2C_1$ values are made according to the method of *Figure 4*, the slope is somewhat less than unity. One notes that $2C_2$ at $\phi_2 = 0.30$ has dropped to only half its value at $\phi_2 = 1.0$ and would not approach zero very rapidly on further lowering of ϕ_2 unless a catastrophic drop in $2C_2$ occurred below $\phi_2 = 0.30$.

It does not appear rewarding at this time to pursue further the implications of equations (5) and (6) regarding dependency of C_2/C_1 and N_c on ϕ_2. With the single exception of the *t*-PPE data of *Figure 3*, there is not sufficient data available to make good estimates of the slopes in log C_2/C_2–log ϕ_2 plots. In many cases adequate characterization parameters and exact procedural details were not given (see Appendix 5 of ref. 10). Finally, there is ambiguity about the parameter r in equation (5); if $r = 1$, the slope should be 3 which was rarely seen; if $r = 0.5$, the slope should be 1.5 which is reasonably close to values of 1–2 observed on several occasions. Moreover, m in equation (4) does vary with $2C_1$ as shown previously.

(4) CORRELATION OF f_e/f WITH AREA PER CHAIN

One hitherto unconsidered factor affecting rubber elasticity is the energy contribution to the total retractive force, commonly expressed as f_e/f. Mark has tabulated values of this ratio for a large variety of elastomers[43]. A prior study of elastic modulus against area[44] showed the desirability of identifying two categories of polymers with respect to conformation; planar and non-planar. Sakurada and Kaji independently arrived at a similar conclusion[45].

Figure 7 is a plot of f_e/f against area in which the planar polymers all lie at the left and show a seemingly marked dependence of f_e/f on area whereas only a mild such dependence is indicated for the non-planar polymers. Area in this example may be no more than a convenient ordering parameter. Decreasing chain area leads to an increase in: C_2/C_1; entanglements per chain; intermolecular forces; and tendency to crystallize. Only N_c and σ decrease with decreasing chain area, where σ is the chain stiffness parameter[46]. Negative values of f_e/f may well be associated with a force-induced tendency to crystallize, with a resultant spontaneous elongation. Liberman *et al.*[47], studying stress optical coefficients,

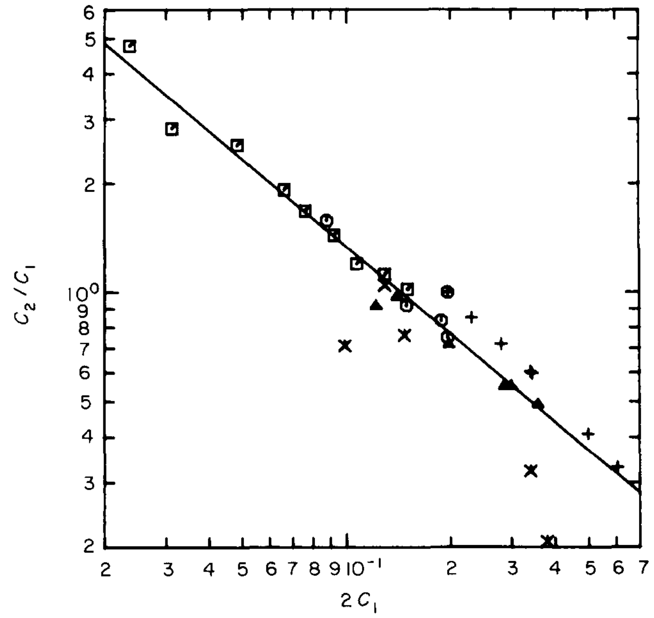

Figure 6 C_2/C_1 plot against $2C_1$ (MPa) for vulcanized natural rubber (*hevea brasiliensis*). Regression line fitted to data of Bristow[38], □; Ciferri and Flory[39], ○; Mullins[40], △; other data plotted only are Gumbrell[32], +; and Allen *et al.*[41], ×. This plot supersedes Figure 3 of ref. 10

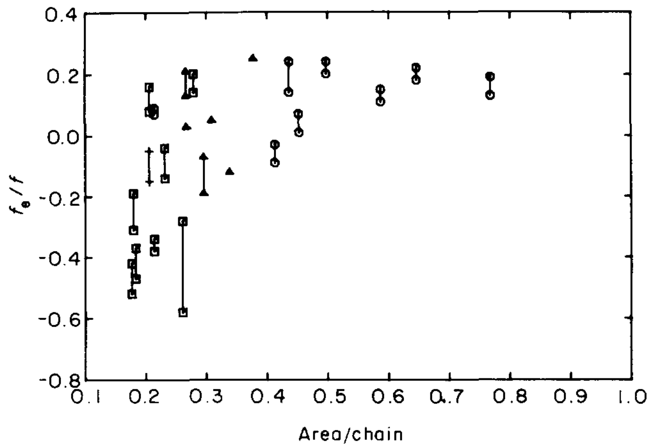

Figure 7 Fractional contribution of elastic energy, f_e, to the total retractive force, f, as a function of area per chain in nm^2. Vertical bars represent extreme values. All data tabulated by Mark[43]. Planar conformations, □ (1976) and + (1973); non-planar conformations, ○ (1976) and △ (1973)

refer to a stress induced correlation of orientations which was very high for linear PE even in hydrocarbon diluents.

There have been divergent views expressed in the literature about the origin of the f_e term. Van der Hoff[48] concluded that an average attraction between stress-aligned chains was responsible for the deviation from entropic theories of elasticity. Allen *et al.*[41] and Shen [49] concluded that f_e had an intrachain origin. Van der Hoff studied undiluted high *cis* content PBD which has an area ≈ 0.18 nm^2. The latter two studied diluted natural rubber which has an area of ≈ 0.28 nm^2 in the undiluted state. Both are planar polymers. Liberman *et al.*[47] found a high correlation of molecular orientation for linear PE both in the bulk and diluted by various hydrocarbons. This seems consistent with the large negative f_e/f for PE.

(5) SUMMARY AND CONCLUSIONS

Numerous conflicting views about the origins of C_1 and C_2 exist:

(1) C_2 due to physical rather than phantom chains[29–32];
(2) internal energy changes affect C_2[50];
(3) entropic origin of both C_1 and C_2[41];
(4) C_2 due to intermolecular order[2,3,26–28,51–54];
(5) physical entanglements for C_2[22–25,55–57] and chemical entanglements for C_1[56,57];
(6) a secondary role for entanglements in C_2[26]; and
(7) entanglements play no role[33].

It was our initial expectation that the techniques based on cross-sectional area introduced herein might resolve some of these conflicts. This has not materialized, in large part from lack of suitable data in the literature.

We have employed several new approaches trying to resolve some of the conflicting views about molecular origins of the C_2 term.

According to our analysis presented earlier, based on equations (2) and (3), it is apparent that both intermolecular forces and entanglements per chain increase as the cross-sectional area per chain, or the intermolecular distances, decrease and *vice versa*. We consider that equations (2) and (3) are independently correct. It then follows that equation (4) is functionally correct. Equation (6), which follows from equation (4) is also functionally correct. Yet an attempt to apply equation (6) to several elastomers vulcanized in solution and then extracted does not support equation (6) and the entanglement concept.

This does not vitiate the validity of equations (2) and (3). The data on $2C_1$ and $2C_2$ leading to equation (2) deliberately avoided cases of vulcanization in the dilute state. Likewise, N_c values used refer to the bulk state and not to a diluted state. It may be necessary to develop two new relationships, $C_2/C_1=F_1(A,\phi_2)$; $N_c=F_2(A,\phi_2)$ and relate C_2/C_1 to N_c at fixed ϕ_2.

We must emphasize that experiments in the literature concerning vulcanization during dilution followed by extraction were not designated to test out equations (5) and (6); and hence the necessary data are not usually available. The *t*-PPE data of Meissner and Klier seen in *Figures 2* and *3* constitutes a model set of data but still lacks information on the dependence of N_c on dilution.

The numerical relationship of equation (6) provides in principle a new way to explore the role of chain entanglements. Properly designed experiments are needed. One factor which requires experimental clarification is the effect of sol removed during the extraction step of vulcanizates prepared in the presence of diluents. An obvious comparison is that of vacuum drying vs. solvent extraction to remove diluent.

Finally, attention was directed to three instances in which C_2/C_1 did not seem to approach zero as $\phi_2 \to 0$: ethylene–propylene elastomer[34]; *cis*-polybutadiene[35] and *trans*-polypentenamer[25]. A catastrophic drop in C_2/C_1 at very low ϕ_2 cannot be ruled out. Even more disturbing is the fact that two sets of workers come to opposite conclusions as seen in *Figure 5* for *cis*-PBD.

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This material was presented in part by R.F.B. at the International Rubber Symposium, Kiev, USSR, on 10–14 October 1978. An uncorrected version appeared in full in the Abstract Booklets of that meeting: Section A on 'Modern Problems of Rubber Physics and Chemistry', specifically Section A$_1$. The present manuscript has been corrected and updated from that first version.

APPENDIX I

Log (C_2/C_1)–Log $2C_1$ plot for natural rubber

An earlier plot of $\log(C_2/C_1)$ vs. $2C_1$ for NR (Figure 3 of ref. 10) required revision because we had inadvertently omitted the data of Bristow[38] in the low to medium range of $2C_1$ and that of Mullins[40] at higher values of $2C_1$. The data were taken directly from the tabulation in Table IV of Mark[7] which includes, in addition to results of Bristow and of Mullins, the data of Ciferri and Flory[39] as well as that of Gumbrell, Mullins and Rivlin[32]. The linear least squares regression line was shown in *Figure 6*. The parameters of this line are listed in *Table 5*. This regression line is based only on the three sets of data; Bristow, Ciferri and Flory, and Mullins. The Gumbrell *et al.*[32] data points are clearly above the regression line.

Table 5 Parameters of straight line in *Figure 7* for *Hevea Brasiliensis*[a] [$\log C_2/C_1 = \alpha + \beta \log 2C_1$]

α	β	R^2 [b]	SE[c]
−0.67424	−0.799	0.971	0.0444

[a] Based on $2C_1$ and $2C_2$ data (N mm^{-2}) of Bristow[38], Ciferri and Flory[39], and Mullins[40]. Data of Gumbrell *et al.*[32] and of Allen *et al.*[41] are plotted but not used in the linear least squares regression analysis

[b] Correlation coefficient of regression

[c] Standard error in log C_2/C_1

Also shown are five data points given by Allen, Kirkham, Paget and Price[41]. Mark[7] did not cite this data, presumably because of its lack of internal consistency. This data set behaves as if the vulcanizates had been extracted with a solvent to remove sol. This procedure has been shown (Figure 8 and related discussion of ref. 10) to reduce C_2/C_1 values for PBD. The laboratory from which this work came[58] has used solvent leaching of vulcanizations on other occasions.

Revised values of C_2/C_1 are readily calculated from the equation of the line at $2C_1 = 0.1$, 0.2 and 0.3 MPa: these values are respectively 1.334, 0.766 and 0.5541. The middle value appears in *Table 1* of this paper. These values replace the ones given in Table I of ref. 10. The good linearity of the line is shown in part by $R^2 = 0.971$. But in addition, the computer print-out (not shown) of residuals/standard error is reasonably random about zero, with 80% of the 20 data points within ±1 standard error, 90% of the points within ±2 standard error. A residual is defined as $\log C_2/C_1$ (observed) − $\log(C_2/C_1)$ (calculated).

APPENDIX 2

The vulcanizates of Meissner and Klier

We have commented that the *t*-PPE data of Meissner and Klier[25] was very complete in terms of range in $2C_1$ values and experimental variables reported. Part of these data was shown in *Tables 2* and *3* and *Figures 2* and *3*. A further analysis of the complete data set appears in *Figure 8* which compares C_2/C_1 vs. $2C_1$ for the extracted and non-extracted vulcanizates.

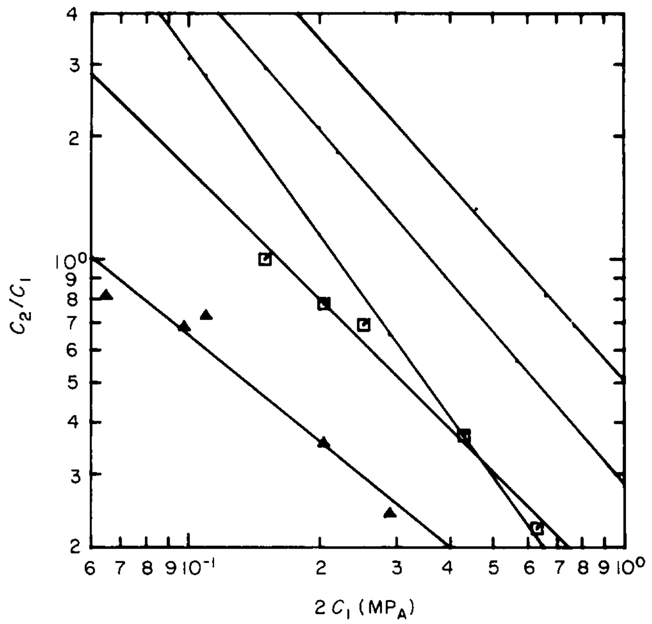

Figure 8 C_2/C_1–$2C_1$ plots for *t*-PPE. Top three lines without points are identical to lines in *Figure 2* vulcanized in diluent at $\phi_2 = 0.96$, 0.47 and 0.31, extracted and dried. The bottom two plots show effect of not extracting the diluent. C_1 and C_2 are determined with fractional diluent contents = ϕ_2, namely 0.47, □; and 0.31, ○

The top three lines without data points are repeated from *Figure 2*. The bottom two lines, for $\phi_2 = 0.47$ and 0.31, respectively, show the effect of leaving the paraffin oil diluent in the vulcanizates. Hence this figure permits a comparison of essentially bulk vulcanizate, $\phi_2 = 0.96$, two levels of diluent during vulcanization, and two levels of diluent in these same vulcanizates. The equations of these two lower lines are: $(\phi_2 = 0.47) \log C_2/C_1 = -0.835 - 1.055 \log 2C_1$; $(\phi_2 = 0.31) \log C_2/C_1 = -1.043 - 0.857 \log 2C_1$. In both cases $2C_1$ is in units of MPa. In a single experiment with $\phi_2 = 0.823$ during vulcanization followed by dilution of the vulcanizate (presumably with paraffin oil) to 0.152, C_2 was zero. One further check was made by us: pairs of values of ϕ_2 and $2C_2$ (at $2C_1 = 0.2$ MPa) for non-extracted vulcanizates could be taken from *Tables 1* and *2* as follows: $\phi_2 = 0.251$, $2C_2 = 0.3$ MPa; 0.31 and 0.73; 0.47 and 0.76; and 0.96 and 5.8 MPa. A log–log plot of $2C_2$ (at $2C_1 = 0.2$ MPa) against ϕ_2 had a slope very close to 2, with some downward concavity as in *Figure 3*, where the extracted sample for $2C_1 = 0.2$ (not shown) has a slope of about unity, concave downwards.

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