

Network Characterization From Stress-Strain Behavior at Large Extensions

M. C. MORRIS,*
*Institute of Rubber Research,
University of Akron, Akron, Ohio*

Synopsis

The stress-strain properties of natural rubber and synthetic *cis*-polyisoprene vulcanizates have been investigated over a large range of extensions. The results are in qualitative agreement with those of Mullins, in that the upturn of a Mooney-Rivlin plot is ascribed to finite extensibility effects. It is further found that the stress-strain curves can be adequately described by a modification of existing non-Gaussian theory. Analysis of the curves shows significant finite extensibility effects even at extensions well below the upturn. Thus, division of stress-strain curves into Gaussian and non-Gaussian regions is to be avoided. Values for n , the number of statistical segments between crosslinks, were calculated using the proposed treatment. The values of n found were relatively unaffected by temperature. Further, the molecular weight of a statistical segment was found to be about the same for synthetic *cis*-polyisoprene as for natural rubber despite differences in the crystallization behavior. Crystallization effects are therefore thought to be of little importance in determining the position of the upturn. The equivalent statistical segment was found to be 4.3 isoprene units for natural rubber and *cis*-polyisoprene.

INTRODUCTION

The Gaussian statistical theory of rubberlike elasticity yields a stress-strain relation for rubber in simple extension which is independent of the lengths of the network chains. The equation is:

$$f = A_0 \nu k T (\lambda - \lambda^{-2}) \quad (1)$$

where f is the force of retraction at an extension ratio λ , k is the Boltzmann constant, and T is the absolute temperature. A_0 is the cross-sectional area in the unstrained state. The parameter ν , the number of effective network chains per unit volume, is the only network parameter involved.

Investigation of the most general relations for the change in stored energy with deformation gives the Mooney-Rivlin equation¹ as a first approximation:

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

where C_1 is associated with the statistical theory term $1/2 \nu k T$, and the origin of the C_2 term is unknown. For the sake of simplifying equations,

* Present address: Research Division, Goodyear Tire and Rubber Co., Akron, Ohio.

let $\phi = f/[A_0(\lambda - \lambda^{-2})]$. According to eq. (2), a plot of ϕ versus $1/\lambda$ should lead to a straight line having a slope of $2C_2$ and an intercept of $2C_1$. While agreement at moderate extensions is good, the stress-strain behavior of typical vulcanizates deviate from linearity at high extensions. This is shown in Figure 1A.

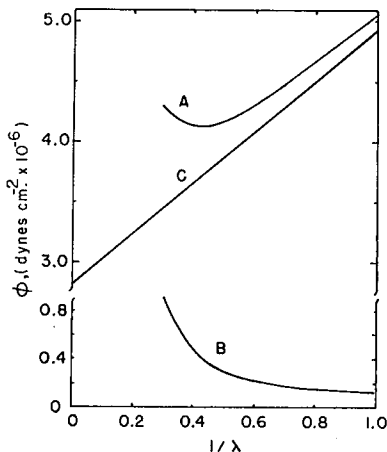


Fig. 1. Division of a stress-strain curve into component terms: (A) experimental relation, natural rubber, 25°C.; (B) finite extensibility component; (C) $(2C_1 + 2C_2/\lambda)$ term.

A more accurate statistical treatment is obtained by considering that each chain is constructed of a finite number of statistical segments. One such treatment leads to the non-Gaussian work function given by Treloar,² which upon differentiation by λ yields:

$$f = A_0 \nu k T (\lambda - \lambda^{-2}) \left[1 + \frac{3}{25n} (3\lambda^2 + 4\lambda^{-1}) + \frac{297}{6125n^2} (5\lambda^4 + 8\lambda + 8\lambda^{-2}) + \dots \right] \quad (3)$$

where n is the average number of statistical segments between crosslinks. The quantity in brackets will hereafter be referred to as $f(\lambda, n)$. Equation (3) may be rewritten as:

$$\phi = 2C_1 f(\lambda, n) \quad (3A)$$

Mullins⁴ has used eq. (3) to calculate conjugate values of λ and n which give the deviation due to finite extensibility the value 2.5% of C_1 . The molecular weight between crosslinks, M_c , is directly proportional to n . The proportionality constant is the molecular weight of a statistical segment. Thus, the extension λ^* , giving this deviation for an experimental vulcanizate, can be related to M_c . Good agreement in this proportionality has been demonstrated by Mullins.

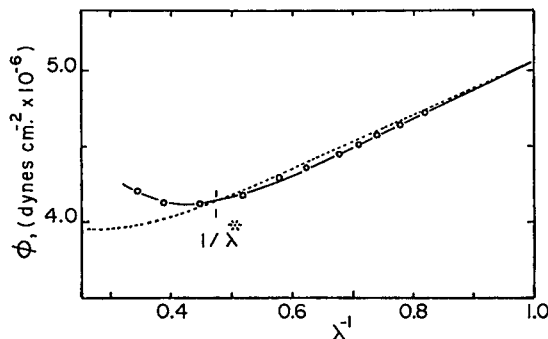


Fig. 2. Experimental and predicted stress-strain relation for a natural rubber vulcanizate (Sample II-3): (—) experimental; (---) calculated by using finite extensibility term from Mullins' approach.

The predicted ϕ versus $1/\lambda$ curve from Mullins' treatment can be found by adding the deviation due to finite extensibility to the extended linear low extension portion of the experimental curve. Such a curve is shown in Figure 2 for a typical natural rubber vulcanizate. The finite extensibility added was $2C_1[f(\lambda, n)/f(\lambda, n)_{\lambda=1} - 1]$ as used by Mullins.⁴ A poor fit is found with the predicted curve crossing the experimental one at λ^* . The value of n , as determined by this treatment, is obviously dependent upon the magnitude of the deviation chosen for λ^* . Unique values for n cannot be expected.

A more suitable treatment can be given. Using eq. (3) with an additional term of the Mooney form, we have:

$$\phi = 2C_1 f(\lambda, n) + (2C_2/\lambda) \quad (4)$$

The terms $2C_1$ and $2C_2$ are not the experimental intercept and slope. The predicted slope of a plot of ϕ versus $1/\lambda$ is easily found by differentiation of eq. (4) by $1/\lambda$:

$$\frac{d\phi}{d(1/\lambda)} = 2C_1 \frac{d}{d(1/\lambda)} f(\lambda, n) + 2C_2 \quad (5)$$

At the minimum value of ϕ the slope is zero and:

$$\frac{2C_2}{2C_1} + n^{-1} \frac{6}{25} (2 - 3\lambda^3) + n^{-2} \frac{297}{6125} (-20\lambda^5 - 8\lambda^2 + 16\lambda^{-1}) = 0 \quad (6)$$

Assuming that $2C_1$ and $2C_2$ are approximately given by the experimental intercept $2C'_1$, and slope $2C'_2$ and assuming that terms beyond the n^{-2} term of eq. (6) are negligible, an approximate solution for n can be obtained by use of the quadratic formula. The approximate value of n , along with two experimental points allow the calculation of better values for $2C_1$ and $2C_2$ from eq. (4). Successive approximations permit calculation of the n value giving the best fit to the experimental data. The terms $2C_1$ and $2C_2$ may be viewed as the intercept and slope of a ϕ versus $1/\lambda$ plot for hy-

pothetical vulcanizate having infinitely flexible chains. The experimental curve *A* in Figure 1 is described by sum of curves *B* and *C* where:

$$\phi_B = 2C_1 [f(\lambda, n) - 1]$$

$$\phi_c = 2C_1 + (2C_2/\lambda)$$

The finite extensibility term, curve *B*, is seen to be of importance even at relatively low extensions for a typical vulcanizate. This factor is the cause of the shortcoming observed in Mullins' treatment. The extrapolated low extension portion of the stress-strain curve is not a suitable base line from which a finite extensibility deviation can be measured. Even the low extension portion of the curve contains finite extensibility effects.

EXPERIMENTAL

Vulcanizates of natural rubber and synthetic *cis*-polyisoprene were prepared with the use of dicumyl peroxide as the curing agent. The initial molecular weights, M_n , were calculated from intrinsic viscosities by use of the equation:⁴

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

Except where otherwise noted, a table-model Instron tester was used to obtain the stress-strain behavior of the vulcanizates. Most of the natural rubber test pieces were of standard T-50 size. Later measurements made use of strips $\frac{1}{4} \times 3 \times 0.030$ in. in order to determine more accurately the cross-sectional areas and the original lengths. The rate of strain was 0.2 in./min. Preliminary investigations showed that the value of n calculated was insensitive to the rate of strain below about 50%/min. For comparison, a loaded pan technique was used for several samples. Weights were added at intervals of 5 min. While the Instron tester gave a more reproducible curve, no difference in results was observed between the two methods.

Natural Rubber at 25°C.

The stress-strain behavior of several dicumyl peroxide vulcanizates of natural rubber are shown in Figure 3. Samples I-1 and I-2 contain 1 part dicumyl peroxide per 100 parts rubber. Samples of set II contain 2 parts dicumyl peroxide per 100 parts rubber. Vulcanizates within each set were subject to simultaneous curing in sections of the same mold. Thus, the samples differ only in primary molecular weight. The curing conditions were 60 min. at 150°C. The minima of the curves are seen to be unchanged by initial molecular weight. However, increase in the degree of vulcanization shifts the minima to lower extensions as previously shown by Mullins. Table I gives the intercept $2C'_1$ and slope $2C'_2$ from ϕ versus $1/\lambda$ plots for these vulcanizates. The values of M_c given have been calculated from $2C'_1$ by use of Mullins^{3,4} empirical equation. Mullins⁴ also gave a method

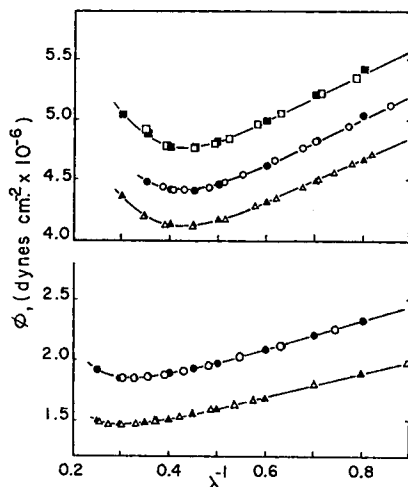


Fig. 3. Experimental and predicted stress-strain curves for natural rubber (25°C.): upper curves: (□) II-1, (○) II-2, (△) II-3; lower curves: (○) I-2, (△) I-3. Solid points calculated from eq. (4) by using appropriate values of n .

for calculating n from the upturn of a Mooney-Rivlin plot. Table II compares values of n calculated from the two treatments. Using Mullins' approach, the statistical segment length is 1.1 isoprene units, which is in agreement with Mullins' results. Values of ϕ predicted by eq. (4) give

TABLE I
Network Parameters for Natural Rubber Vulcanizates

Vulcani- zate ^a	$M_n \times 10^{-5}$	M_c	$2C'_1 \times 10^{-6}$	$2C'_2 \times 10^{-6}$
I-1	1.31	8830	1.55	1.30
I-2	1.18	8820	1.44	1.09
I-3	1.08	9350	1.09	1.01
II-1	2.15	5478	3.82	1.90
II-2	1.59	5505	3.66	1.88
II-3	1.25	5644	3.40	1.77

^a Set I, 1 phr dicumyl peroxide; set II, 2 phr dicumyl peroxide; measurements at 25°C.

TABLE II
Comparison of n Values from Mullins' and Present Approach for Natural Rubber Vulcanizates

Vulcanizate	λ^*	$n(\lambda^*)$	λ , min.	$n(\lambda)$, min.
I-2	2.78	130	3.08	30.5
I-3	2.82	134	3.23	32.0
II-1	2.30	81	2.35	17.7
II-2	2.22	75	2.41	18.1
II-3	2.27	79	2.41	19.5

good fit to the experimental curves with appropriate values of n , as shown in Figure 3. The statistical segment length calculated by the proposed treatment is 297 molecular weight units or 4.3 isoprene units.

Natural Rubber at 75°C.

It has been proposed, at times, that the upturn in the Mooney-Rivlin plot may be due to the onset of crystallization.⁵ In order to check the importance of this factor, a stress-strain experiment was performed at 75°C., a loaded pan technique being used. The sample was kept under nitrogen as a precaution against oxidative degradation. Use of the extension at ϕ minimum gave an n of 16.6. The fit of the curves is again good. Table III compares $2C'_1$, $2C'_2$, and n at 25 and 75°C., revealing only

TABLE III
Effect of Temperature on n (Sample II-3)

Temp., °C.	$2C'_1 \times 10^{-6}$	$2C'_2 \times 10^{-6}$	n
25	3.40	1.77	19.5
75	3.92	2.37	16.6

a small change in the calculated value of n . One would expect the degrees of crystallinity at a given extension to differ considerably. The indications are that crystallization is of minor importance in the shape of the upturn.

Synthetic *cis*-Polyisoprene

Samples of Shell Chemical *cis*-polyisoprene were milled and vulcanizates prepared, dicumyl peroxide being used as the vulcanizing agent. Analysis of the stress-strain curves gave values of $2C'_1$, and n as listed in Table IV. As before, excellent fit was provided by eq. (4). Values for M_c physical were calculated by Mullins'⁴ empirical equation by using the parameters for natural rubber. The average found for M_c/n was about 300. This agrees well with 297 found for natural rubber.

TABLE IV
Network Parameters and Segment Weight for Synthetic *cis*-Polyisoprene Vulcanizates

Vulcanizate*	$2C'_1 \times 10^{-6}$	$M_n \times 10^{-6}$	M_c	n	Segment wt.
II-SA-1	2.28	2.73	8665	25.4	326
II-SA-2	1.62	2.73	10087	32.8	307
II-SA-3	1.68	2.73	9916	34.3	289
II-SB-1	2.28	2.62	8219	24.9	330
II-SB-2	1.63	2.62	9988	36.5	273
III-SB-1	3.62	2.62	5686	21.9	259

* Set II, 2 phr dicumyl peroxide; set III, 3 phr dicumyl peroxide; degree of vulcanization varied by change of cure times at 150°C.; measurements at 25°C.

CONCLUSION

Figure 3 shows the extension at the upturn to be independent of initial molecular weight for natural rubber vulcanizates. Figure 3 also shows this extension to vary with the degree of crosslinking. These results are in accord with the findings of Mullins.⁴

It has been found that experimental stress-strain curves can be described by the modified non-Gaussian equation (4) by using the n values calculated by the method proposed here. Thus, the n values are more significant than those found by the λ^* approach. Inspection of the forms and magnitudes of the terms involved in eq. (4) reveals a small but significant contribution to ϕ by finite extensibility even at low extensions. This contribution affects the extrapolation to C_1 on the Mooney-Rivlin plot. Further work will be required to assess this factor properly. In this work, the physical molecular weight between crosslinks has been determined by Mullins' empirical equation. Since C_1 is less than C'_1 , it can be seen that the observed entanglement contribution in Mullins' empirical equation will be somewhat reduced when the effect of finite extensibility is considered. However, this point should be approached with caution since the extrapolation to C_1 depends upon the form of the $2C_2$ term. The origin and form is not yet adequately understood.

Since the finite extensibility term has an appreciable contribution at extensions below the upturn, reference to the onset of finite extensibility or to Gaussian or non-Gaussian regions should be avoided. Gaussian theory provides an apparent fit at low extensions only because the curvature is too small to be noticed and not necessarily because the contribution is insignificant.

Since little change in n was observed when the temperature was raised to 75°C., crystallization effects seem to be of minor importance at the extensions considered for natural rubber. The results of the *cis*-polyisoprene experiments also tend to verify this conclusion. The random length size should be the same for natural rubber and synthetic *cis*-polyisoprene but the crystallizing properties differ greatly.⁶ Within experimental error, the statistical segment sizes were found to be the same, 4.3 isoprene units, for natural rubber and synthetic *cis*-polyisoprene.

A value of 2.8 isoprene units per equivalent statistical segment was found by Kuhn and Kuhn⁷ from viscosity and flow birefringence. A value of 2.2 units was reported by Saunders⁸ from birefringence measurements. Treloar⁹ gives the theoretical value, calculated on a geometrical basis as 0.77 isoprene units. The above values may be compared to 1.1 isoprene units determined by Mullins' treatment of finite extensibility and 4.3 isoprene units determined by the method proposed here. While the value of 4.3 isoprene units is greater than the values previously reported, it is not felt to be unreasonably high. Restrictions to free rotation about bonds as well as other intramolecular interactions affect chain stiffness.

It has not been shown that the effective values of n are number-average

values. If one considers several possible paths connecting two arbitrary points in a random network, one may assume that the path having the shortest contour length will carry the bulk of the load. Thus, the average number of statistical segments, n , is expected to be weighted toward short chains.

The study, while modifying Mullins'⁴ numerical conclusions greatly, confirms the hypothesis that departures from the statistical theory at high extensions are due to the finite extensibility of the network. Agreement is seen not only in the proportionality of M_c values to n values but, also, in the ability of the proposed equation to describe the experimental curve. A more rigorous treatment of finite extensibility must await advancement in understanding the nature of the C_2 term.

This work was supported in part by the Synthetic Rubber Division, Shell Chemical Company. The author is grateful to Dr. M. Morton and Dr. A. N. Gent for helpful suggestions.

References

1. Mooney, M., *J. Appl. Phys.*, **11**, 582 (1940).
2. Treloar, L. R. G., *Trans. Faraday Soc.*, **50**, 881 (1954).
3. Mullins, L., *J. Appl. Polymer Sci.*, **2**, 1 (1959).
4. Mullins, L., *J. Appl. Polymer Sci.*, **2**, 257 (1959).
5. Fox, T. G, P. J. Flory, and R. E. Marshall, *J. Chem. Phys.*, **17**, 704 (1949).
6. Scott, K. W., G. S. Trick, R. H. Mayor, W. M. Saltman, and R. M. Pierson, *Rubber Plastics Age*, **52**, 175 (1961).
7. Kuhn, W., and H. Kuhn, *Helv. Chim. Acta*, **26**, 434 (1943).
8. Saunders, D. W., *Trans. Faraday Soc.*, **52**, 1414 (1956).
9. Treloar, L. R. G., *The Physics of Rubber Elasticity*, Clarendon Press, Oxford, 1958, p. 59.

Résumé

On a étudié les propriétés de traction-tension interne devuleanisats de caoutchouc naturel et de *cis*-polyisoprène synthétiques dans une large domaine d'extension. Les résultats s'accordent qualitativement avec ceux de Mullins en ce sens que la remontée de la courbe de Mooney-Rivlin est attribuée à des effets d'extensibilité limitée. On trouve d'autre part que les courbes de traction-tension interne peuvent être décrites de façon adéquate par une modification de la théorie existante. Une analyse des courbes montre des effets d'extensibilité limitée même aux extensions bien en-dessous de la remontée. Ainsi donc il faut éviter la division des courbes de traction-tension interne en une région gaussienne et nongaussienne. En utilisant le traitement proposé on a calculé les valeurs de n , c.à.d. le nombre de segments statistiques entre les ponts; les valeurs trouvées pour n sont relativement peu affectées par la température. De plus on trouve que le poids moléculaire d'un segment statistique est à peu près le même pour du *cis*-polyisoprène synthétique que pour le caoutchouc naturel malgré les différences dans le comportement en cours de cristallisation. Dès lors on pense que les effets de cristallisation sont de peu d'importance dans la détermination de la remontée de la courbe. On trouve que le segment statistique équivalent est constitué de 4,3-unités d'isoprène pour le caoutchouc naturel et le *cis*-polyisoprène.

Zusammenfassung

Die Spannungs-Dehnungseigenschaften von Naturkautschuk- und synthetischen *cis*-Polyisoprenvulkanisaten wurden in einem grossen Dehnungsbereich untersucht. Die Ergebnisse stimmen qualitativ insofern mit denjenigen von Mullins überein, als die Aufwärtskrümmung im Mooney-Rivlin-Diagramm den Einfluss der endlichen Dehnbarkeit zugeschrieben wird. Es wird weiters festgestellt, dass eine adäquate Beschreibung der Spannungs-Dehnungskurven durch eine Modifizierung der bekannten nicht-Gauss'schen Theorie möglich ist. Eine Analyse der Kurven zeigt schon bei Dehnungen weit unterhalb des Einsetzens der Aufwärtskrümmung den charakteristischen Einfluss der endlichen Dehnbarkeit. Es sollte daher eine Unterteilung der Spannungs-Dehnungskurven in Gauss'sche und nicht-Gauss'sche Bereiche vermieden werden. Werte für n , die Anzahl der statistischen Segmente zwischen zwei Vernetzungsstellen, wurden auf die vorgeschlagene Weise berechnet. Die gefundenen n -Werte zeigten eine verhältnismässig sehr geringe Temperaturabhängigkeit. Ungeachtet der Unterschiede im Kristallisationsverhalten erwies sich das Molekulargewicht eines statistischen Segments bei synthetischem *cis*-Polyisopren und Naturkautschuk als etwa gleich. Es wird daher angenommen, dass Kristallisationseffekte für die Lage der Aufwärtskrümmung nur wenig Bedeutung haben. Als äquivalentes, statistisches Segment wurde für Naturkautschuk und *cis*-Polyisopren 4,3 Isopreneinheiten festgestellt.

Received December 4, 1962