

Relationship Between Maximum Extensibility of Networks and the Degree of Crosslinking and Primary Molecular Weight

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Synopsis

The relationship between network chain concentration and the maximum value of the extension ratio at break is discussed. Experimental data obtained from the literature are then used to test the theoretically derived dependence.

INTRODUCTION

Based on simple theory,¹ it has been predicted that $(\lambda_b)_{\max} = n^\beta$. Here, $(\lambda_b)_{\max}$ is the maximum value of the extension ratio at break, as determined by the value of λ_b at which the failure envelope has infinite slope; n is the number of statistical units per network chain; and $\beta = 1/2$. In order to test this relationship, n must first be expressed in terms of parameters which can be experimentally evaluated. The purpose here is to show how this can be accomplished and, furthermore, to subject the derived theoretical equations to an experimental test, using the data of Smith on values of $(\lambda_b)_{\max}$ as a function of degree of crosslinking for a Viton elastomer.²

The quantity N_0 is defined as the concentration of statistical units per unit volume of effective network chain:

$$N_0 \equiv \frac{n\nu_e'}{f'} \quad (1)$$

where ν_e' is the concentration of effective network chains in the gel and f' is the fraction of network chains which are terminated at both ends by crosslinked units. This definition of N_0 ensures its independence of both the degree of crosslinking and the primary molecular weight. In eq. (1), and hereafter, the primed quantities refer to the gel fraction. In terms of N_0 , eq. (1) becomes

$$(\lambda_b)_{\max} = n^\beta = \left(\frac{N_0 f'}{\nu_e'} \right)^\beta \quad (2)$$

Equation (2) predicts $(\lambda_b)_{\max}$ to vary as $(\nu_e')^{-\beta}$ when f' is held fixed. In general, however, f' will vary with both the degree of crosslinking and the primary molecular weight; thus, in order to use eq. (2) directly, it is necessary to estimate f' . This can easily be accomplished if the relationship between the

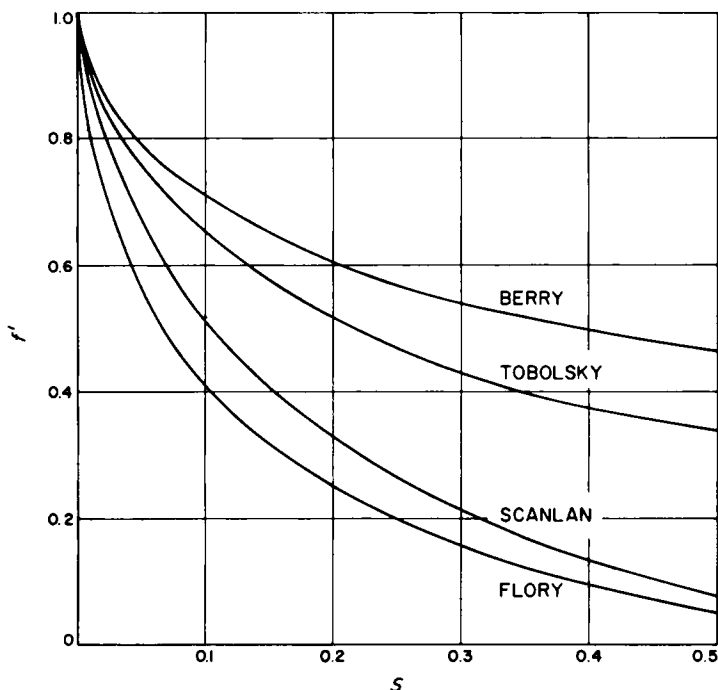


Fig. 1. Variation of the fraction of active gel network as a function of the sol fraction according to the treatments of several theories.

active and inactive portions of the gel, i.e., the free chain end fraction, is known.

Based on differing assumptions and approximations, free chain end corrections have been derived by Flory,³ Berry,⁴ Scanlan,⁵ Tobolsky,⁶ and Mullins.⁷ The relative merits of these different proposals have been discussed by Scanlan.⁵ In Figure 1, plots of f' as a function of the sol fraction s are shown for each relationship except for that of Mullins, since this latter correction closely follows the Tobolsky⁷ equations. For the present purposes, it is sufficient to note that at a given value of s , the Berry expression provides a maximum estimate and the Flory expression a minimum estimate of f' . The Flory expression for f' is given by

$$f' = \frac{1}{\left(1 + \frac{2\rho}{\nu_c' M'}\right)} \quad (3)$$

and the Berry estimate for f' is given by

$$f' = \frac{1}{\left(1 + \frac{\rho}{\nu_c' M'}\right)} \quad (4)$$

where ρ is the polymer density, ν_c' is the concentration of network chains which are terminated at both ends by crosslinked units, and M' is the number-average molecular weight of the primary molecules.

In order to employ eqs. (3) or (4) directly, values of ν_c' and M' must be available. Ordinarily, ν_e' , the concentration of elastically effective chains (which can include a significant contribution from chain entanglements), is experimentally obtained rather than the required ν_c' . However, both Mullins⁸ and Kraus⁹ have shown by means of calibration experiments that ν_e' and ν_c' can be related by an equation of the form

$$\nu_e' = (\nu_c' + a) \left(1 - \frac{b}{\nu_c' M'} \right) \quad (5)$$

where a is the concentration of network chains contributed by entanglements alone at infinite primary molecular weight and b is a constant (generally ~ 2 to 3). If a and b are known for a particular system, then ν_c' values can be calculated directly. However, the values of a and b are available for only a few systems. Nevertheless, even in the absence of specific knowledge of a and b , it is of significance to note that eq. (5) requires $\nu_e' > \nu_c'$ everywhere, and thus ν_e' values can be used as maximum estimates for ν_c' .

It is now necessary to estimate M' . In general, compounding (mixing) and vulcanization of an elastomer might be expected to result in both chain scission and crosslinking occurring simultaneously. The relative extents of these two competing processes will depend on the chemical nature of the elastomer, the nature of the vulcanizing system, and the conditions, e.g., temperature, used to bring about vulcanization. When both scission and crosslinking occur, M' will vary with the degree of crosslinking, since each scission increases the number of primary molecules by one. Thus, in order to evaluate M' , it is necessary first to determine if scission has occurred and, if so, to what extent.

A method of estimating the extents of chain scission is based on sol-gel relationships. Charlesby¹⁰ has derived equations which relate the sol fraction to both the degree of crosslinking and the size and distribution of the primary molecules. In particular, for random chain scission and simultaneous crosslinking of a polymer having a most probable or random molecular weight distribution, Charlesby derived the following equation:

$$s^{1/2}(1 + s^{1/2}) = \frac{p}{\nu_c} + \frac{\rho}{\nu_c M(0)} \quad (6)$$

where p is the concentration of cuts and $M(0)$ is the number-average molecular weight for the whole polymer (sol and gel) before crosslinking. For a random molecular weight distribution, M is related to M' by¹¹

$$M' = (1 + s^{1/2})M. \quad (7)$$

Charlesby has shown that almost any initial distribution will closely approach the most probable after about 1 to 3 random cuts per weight-average chain have occurred. Data points representing specimens at small extents of scission and crosslinking will be expected to diverge from the predicted behavior if the initial distribution is not random. If no scission occurs, then eq. (6) predicts that a plot of $s^{1/2}(1 + s^{1/2})$ versus ν_c^{-1} will be linear with zero intercept and slope equal to $\rho/M(0)$. On the other hand, if scission occurs, then the plot will, in general, yield a curve whose slope at any given value of ν_c^{-1} is $p + \rho/M(0)$. In this case, if $M(0)$ is known from an independent measure-

ment, p can be evaluated at each value of ν_c^{-1} . A particularly simple relationship prevails if p is directly proportional to ν_c , i.e., if $p = K\nu_c$, then the plot of $s^{1/2}(1 + s^{1/2})$ versus ν_c^{-1} will be linear with intercept equal to K and slope equal to $\rho/M(0)$.

In principle, it is thus possible to determine the values of the necessary parameters required in eq. (2). Using the Flory chain end correction, eq. (2) becomes

$$\log(\lambda_b)_{max} = \beta \log \frac{N_0 f'}{\nu_e'} = \beta \log \left[\frac{\nu_c' M'}{\nu_e' (\nu_c' M' + 2\rho)} \right] + \beta \log N_0 \quad (8)$$

and using the Berry estimate for f' ,

$$\log(\lambda_b)_{max} = \beta \log \frac{N_0 f'}{\nu_e'} = \beta \log \left[\frac{\nu_c' M'}{\nu_e' (\nu_c' M' + \rho)} \right] + \log N_0 \quad (9)$$

It is interesting to observe that if $\log(\lambda_b)_{max}$ versus $\log f'/(\nu_e')$ is linear, or approximately so, for both eqs. (8) and (9), then the estimate of β from eq. (8) using the Flory chain end correction will be greater than the estimate of β obtained from eq. (9) using the Berry estimate for the free chain end fraction. Furthermore, if in addition the approximation is made that $\nu_e' = \nu_c'$, as is usually the case in practice, then these estimates for β are the *maximum* estimates.

EXPERIMENTAL

In order to subject eqs. (8) and (9) to experimental test, it is necessary to obtain data on the dependence of $(\lambda_b)_{max}$ on the degree of crosslinking. To ensure that N_0 doesn't vary, it is necessary to obtain the data on a single elastomer since, presumably, N_0 will be a function of the molecular structure of the polymer chain. Fortunately, such data are available in a recent publication by Smith² who reported $(\lambda_b)_{max}$, ν_e' , and s values for a gum Viton elastomer. These data are shown in Table I.

In order to estimate the extent of chain scission which has occurred, the plot suggested by eq. (6) is used with the approximation that $\nu_e = \nu_c$, and these data are shown in Figure 2 as the unfilled points. Except for the data

TABLE I
Selected Properties of Viton Elastomers

Sample	Sol, s	$\nu_e \times 10^6$, moles/cm ³	$c \times 10^6$, moles/g ³	$(\lambda_b)_{max}$	$M \times 10^{-5}$, g/mole	$M' \times 10^{-5}$, g/mole
Original	—	—	0	—	1.54	—
1	0.49	4.6	6.02	19.1	1.49	2.53
2	0.30	16.7	12.0	15.5	1.27	1.97
3	0.18	28.7	18.1	12.6	1.12	1.60
4	0.10	48.6	24.1	8.9	0.94	1.24
5	0.075	61.4	30.1	7.9	0.86	1.10
6	0.036	118	60.2	5.7	0.61	0.72

^aConcentration of curing agent N,N'-dicinnamylidene-1,6-hexanediamine in moles/g of elastomer; ρ for Viton taken as 1.84 g/cm³.

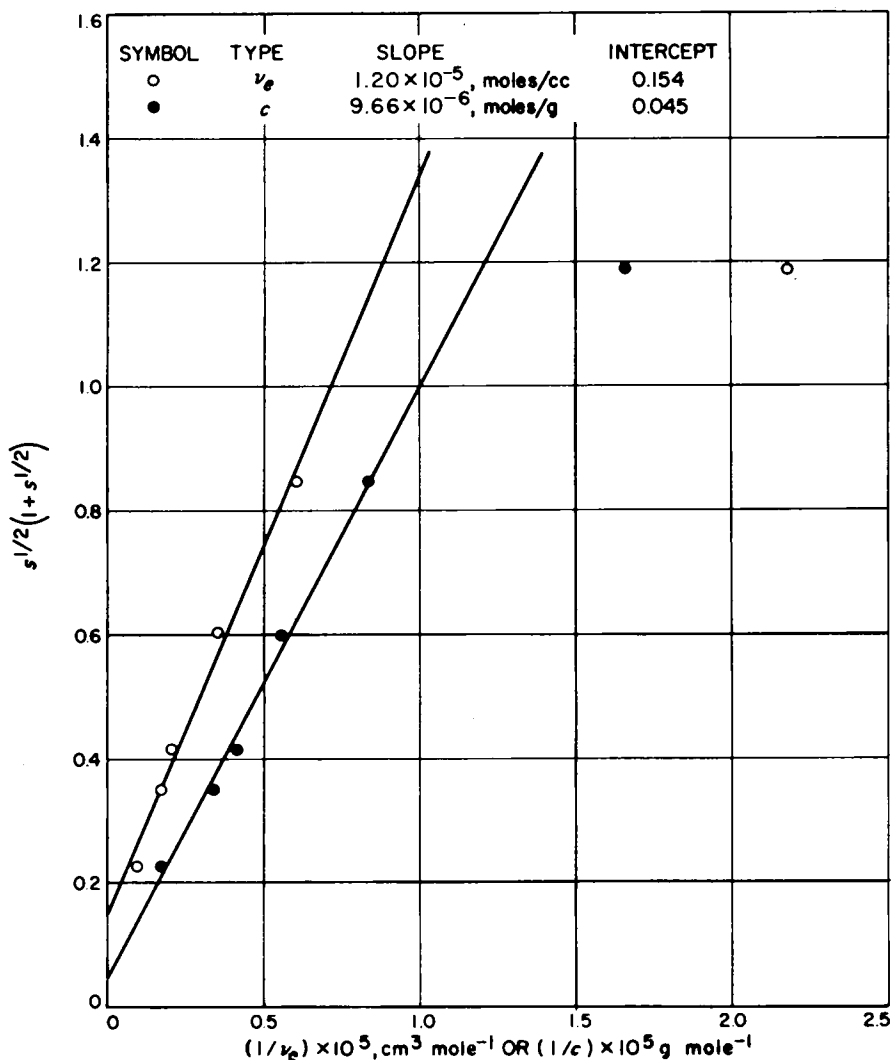


Fig. 2. Variation of the sol fraction $s^{1/2}(1 + s^{1/2})$ as a function of ν_e^{-1} (○) and as a function of c^{-1} (●) for a series of Viton elastomers.

point representing the lowest degree of crosslinking the data can be reasonably represented by a linear relationship. The line shown has been fitted by the least-squares technique, and the slope and intercept are 1.20×10^{-5} moles/cm² and 0.154, respectively. According to eq. (6), linearity implies that the number of cuts p is directly proportional to ν_e , i.e., $p = 0.154 \nu_e$. Since $p = N_i - N(0)$, where N_i is the concentration of primary molecules present in the i th sample after crosslinking and scission have occurred and $N(0)$ is the initial concentration, it is now possible to estimate M for each sample, and these values are listed in Table I. It is of interest to note that, provided the $s^{1/2}(1 + s^{1/2})$ -versus- ν_e^{-1} relation is linear also, these values of M are maximum estimates since $\nu_e > \nu_c$ always, and ν_e was used to estimate ν_c .

In this regard, it is of interest to apply eq. (6), using the concentration of amine curing agent as an estimate of ν_c . If the plausible assumption is made that the concentration of amine, c , is proportional to the number of crosslinks generated, i.e., $c = k\nu_c$, then a plot of $s^{1/2}(1 + s^{1/2})$ versus c^{-1} should be linear

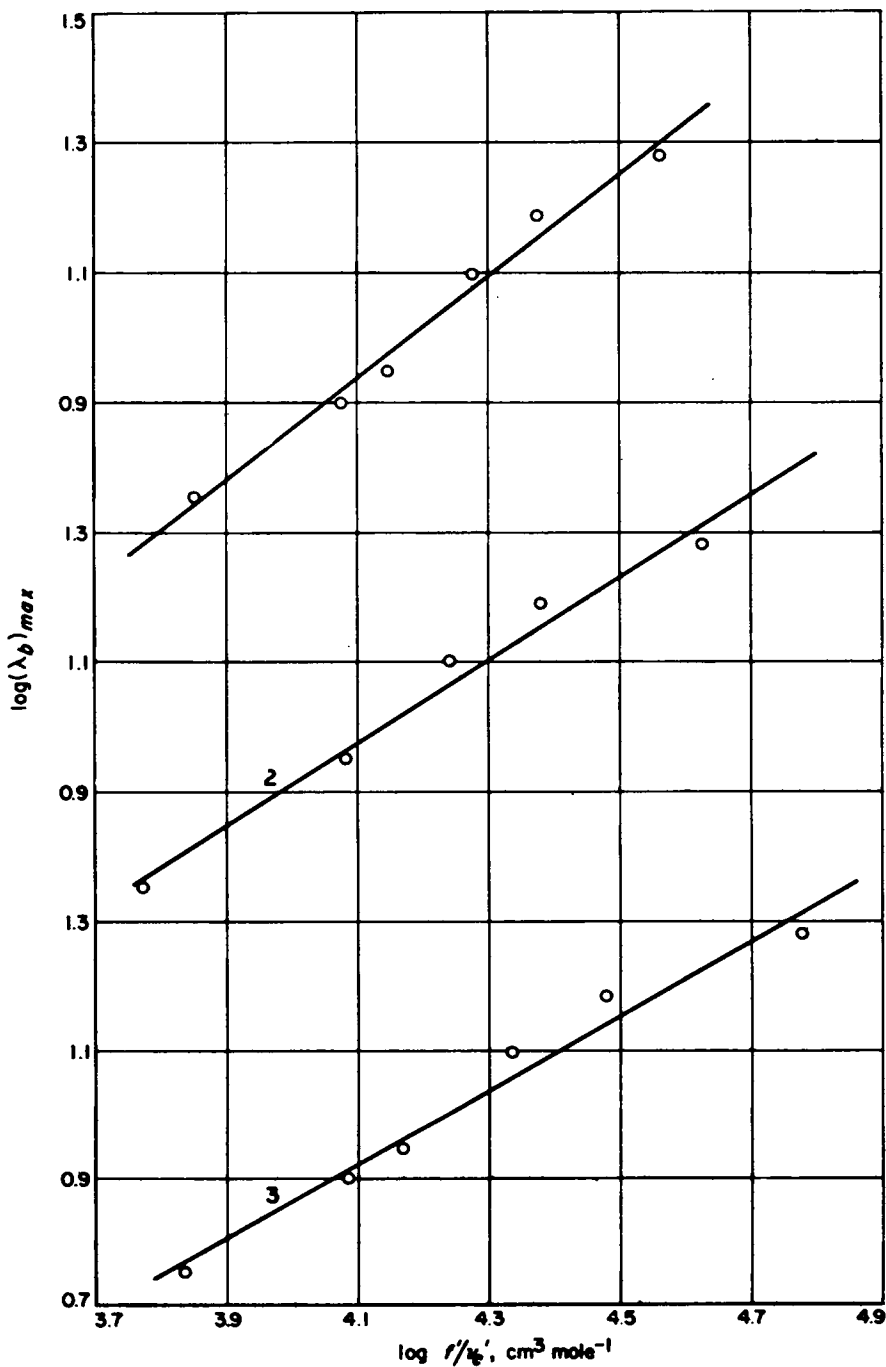


Fig. 3. Dependence of $\log(\lambda_b)_{\max}$ on $\log f'/\nu_e'$ for Viton data of Smith.

also with slope $\rho k/M(0)$ and intercept ρk . These data are the filled points in Figure 2; the line shown was fitted by the least-squares technique, which provided a value of the slope and intercept of 9.66×10^{-6} moles/g and 0.045, respectively. The significant point here is that this plot, like that using ν_e , is linear also. A linear relationship between ν_e and c was obtained by Novikov from studies of Viton elastomers vulcanized by hexamethylenediamine.¹²

It is also of interest to obtain estimates of k . A maximum estimate can be obtained by assuming that no chain scission occurs during compounding; under this condition, $M(0) = 2.4 \times 10^5$ g/mole, which leads to $k = 1.25$. On the other hand, two estimates of the minimum value of k can be obtained; in one, setting $\nu_e = \nu_c$ leads to a minimum estimate for $M(0)$ which provides a minimum estimate for $k = 0.86$; in another, the intercept values from Figure 2 provide $k = 0.54$, in good agreement with the value obtained from the slope. Hence, $0.54 \leq k \leq 1.25$. For a quantitative crosslinker, $k = 2$. For Viton vulcanized with hexamethylenediamine, Novikov's data lead to a maximum estimate of $k = 1.23$.

Having evaluated the various intermediate quantities required, it is now possible to subject the theoretical eqs. (8) and (9) to an experimental check. Figure 3 shows $\log (\lambda_b)_{\max}$ versus $\log f'/\nu_e'$. In curve 1, the data are plotted according to eq. (8), assuming that $\nu_e' = \nu_c'$ and $M' = M = 2 \times 10^5$ g/mole. The line was fitted by the least-squares technique, which provides $\beta = 0.784$. Since $\nu_e' > \nu_c'$ and $M' > M$, this value of β is the largest estimate. Curve 2 is a plot of eq. (8), assuming also only $\nu_e' = \nu_c'$; the least-squares estimate of $\beta = 0.64$. Curve 3 is a plot according to eq. (9), assuming that $\nu_e' = \nu_c'$; the least-squares estimate of $\beta = 0.58$. Since $\nu_e' > \nu_c'$ always, these estimates of β are the *maximum* estimates, and the use of ν_c' itself rather than ν_e' would yield smaller values of β closer to the theoretical one of $1/2$. Hence, the available experimental data indicate that eq. (2) is a good approximation.

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