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A. L. Andrady[a]
[a] Department of Chemistry, University of Cincinnati Cincinnati, Ohio

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Significance of Network Chain-Length Distribution in Chemical Stress Relaxation Studies

A. L. ANDRADY

Department of Chemistry
University of Cincinnati
Cincinnati, Ohio 45221

ABSTRACT

The theoretically expected network chain-length distribution for networks where the cross-link points are randomly distributed in the bulk of the material would contain a significant fraction of network chains which are much shorter than the average chain length. The contribution of these very short chains to the stress born by a network is an important consideration in chemical stress relaxation studies. It is proposed that by use of a gamma distribution function as a "functional" network chain-length distribution, the effect of such short network chains might be taken into account in deriving stress-time expressions for chemical stress relaxation studies. While this procedure yields a simple expression for the fractional residual stress at a given extent of scission, the error involved in neglecting the effect of the chain-length distribution appears to be small.

The theory of chemical stress relaxation seeks to quantitatively explain the time dependence of the fractional residual stress in a vulcanizate test-piece maintained in uniaxial extension under conditions where the change in stress occur mainly due to chemical reactions taking place in the test-piece. Before such quantification is attempted two problems need to be resolved.

1. How can the network parameters (the concentration of the elastically effective network chains, in particular) of the test-piece of the vulcanizate be related to the stress in the test-piece?

2. How does the concentration of the effective network chains in the vulcanizate vary with the number of scission events which take place within it? This requires an expression of the following form to be obtained:

$$\frac{N[t]}{N[0]} = \psi(q) \tag{1}$$

where $N[t]$ and $N_i 0]$ refer to the concentration of the elastically effective network chains at zero time and at time t, respectively, and q is the number of scission events which has occurred.

Of the two considerations, the former can be more easily handled. The statistical theory of rubberlike elasticity obtains an equation of the following form for rubbery networks [1]:

$$f = NkT\theta(\lambda) \tag{2}$$

where λ is the extension ratio and f is the stress in the test-piece. Regardless of the exact nature of the functional dependence of the stress upon the extension ratio, λ, the above relationship yield $f[t]/f[0] = N[t]/N[0]$ at constant temperature.

The second consideration requires some model of the network to be adopted for the purpose of deriving a relation between the quantities $N[t]/N[0]$ and q. Such a relationship might then be translated into a stress-time equation by making use of an appropriate kinetic expression for the scission process. In most instances the chemistry of the scission process in aging polymers is not well understood and the kinetics of the scission needs to be assumed. The use of different models for the network chain-length distribution in deriving such equations is of interest here.

Tobolsky et al. [2] derived the following expression analogous to Eq. (1).

$$\frac{N[t]}{N[0]} = \exp(-q/N[0]) \tag{3}$$

However, Eq. (3) was derived using a mathematical simplification which in effect implies that all the network chains in the network carry the same number of sites capable of undergoing scission (i.e., that the network chains are homogeneous).

The more realistic case is that relating to a network where the cross-link points are randomly distributed in the network. This would give rise to network chains of a variety of different lengths. This case has been considered by Berry et al. [3] who showed that the fraction F_x of network chains of length x units in such a network may be closely approximated by

$$F_x = \exp(-x/\ell)\, \ell^{-1} \tag{4}$$

where ℓ is the average number of units per network chain (i.e., $\ell = \bar{x}$, the average chain length).

An expression relating the average number of cuts per network chain, c, to the fraction of uncut network chains at time t, $N[t]/N[0]$, may be obtained by using Eq. (4). The probability of an x-long network chain being uncut when the average number of cuts (scissions) per network chain is c may be approximated as follows. The required probability P is given by

$$P = (1 - q/N[0])^x \simeq \exp(-xc/\ell) \tag{5}$$

where $c = q/N[0]$. Then

$$N[t]/N[0] = \int_0^\infty F_x \exp(-xc/\ell)\, dx = (1 + c)^{-1} \tag{6}$$

Using this result in Eq. (2) gives

$$f[t]/f[0] = (1 + c)^{-1}$$

The following discussion examines the assumptions made in the above derivation regarding the distribution of network chain lengths in the network.

EFFECT OF HETEROGENEITY OF NETWORK CHAINS ON STRESS-STRAIN MEASUREMENTS

Figure 1 shows a plot of F_x versus x for two networks. The curves thus represent smoothed-out frequency polygons of the network chain lengths. In reality, the function F_x should be a discrete one. However, the continuous function given here closely approximates the expected discrete distribution and is used for case of manipulation. The plot in Fig. 1 shows a significant proportion of short network chains

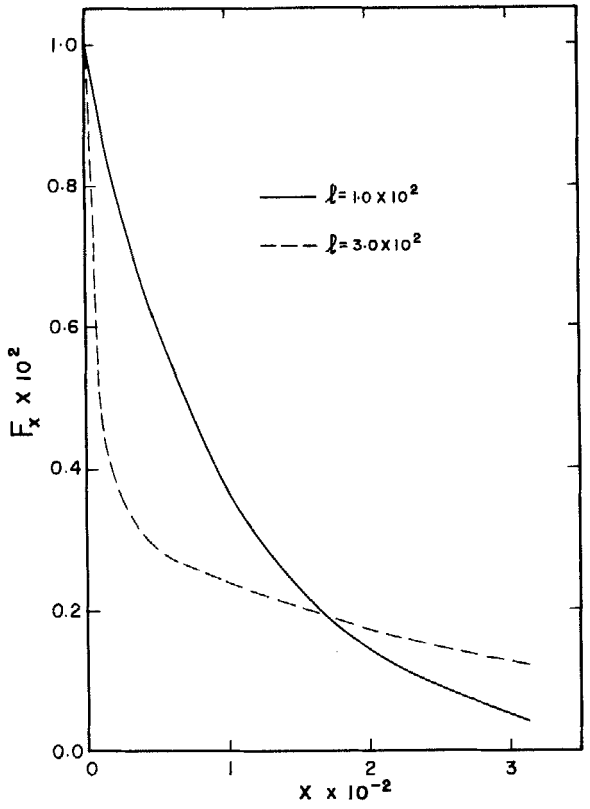

FIG. 1. Theoretical network chain-length distributions for networks where the cross-link points are randomly distributed in the bulk of the network. The average network chain-lengths are indicated.

to be present in a network where the cross-links are randomly distributed. Therefore the question of whether the elastic effectiveness of a network chain depends upon the chain length is a relevant one. In the theories of chemical stress relaxation available at present, an effective network chain has been implicitly defined as any length of stress-bearing network chain extending between two cross-links. Thus all such chains regardless of their length has been considered equally effective. However, it is likely that this might not be the case in networks containing a significant fraction of relatively short network chains.

Consider the qualitative model suggested in Fig. 2. The two adjacent cross-links A and B are separated by a short network chain

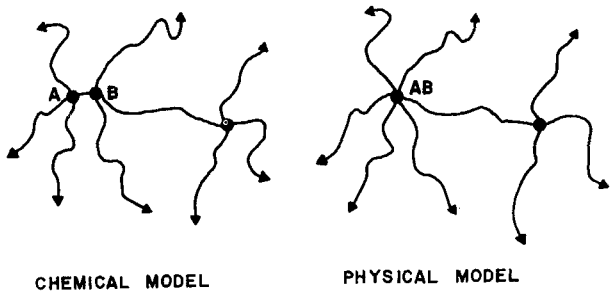

FIG. 2. The chemical and physical models for a pair of adjacent cross-link points, A and B, separated by a network chain very much shorter than the critical network chain length.

of length h units. If, for instance, h is equal to unity, it is virtually impossible for the two cross-links to act independently in a strained network. The two tetrafunctional cross-link points would probably act as a single hexafunctional cross-link point. The physical model referred to in the figure would then be the functional entity. However, as the value of h is gradually increased, the cross-links will become progressively independent of each other. Finally, when h is sufficiently large (i.e., when $h = \mu$, where μ is the critical chain length), the constraints placed upon one cross-link by the stresses on the chains attached to the other cross-link would be minimal, making the two cross-links independent of each other and fully elastically effective.

Such a phenomenon would tend to increase the effective functionality of the cross-links concerned and would also reduce the number of effective cross-links in a network. The net result of such changes would be to increase the functional molecular weight between the cross-links, M_c, in the network. Very little experimental work has been done on networks of well-characterized network chain-length distributions. However, the end-linked model network systems afford a means of comparing the experimentally obtained M_c values with the independently determined values of M_c. Stress-strain studies using such networks containing known fractions of shorter network chains might be employed to quantify the effect of the network chain-length distribution on stress-strain properties. Some recent work by Mark [4] on model networks of PDMS did show an increase in the experimentally determined M_c (from $2C_1$ measurements) with the increase in the fraction of very short network chains in the network.

OBTAINING CORRECTION FACTORS FOR THE EFFECT OF NETWORK CHAIN LENGTH DISTRIBUTION

Equation (4) gives the fraction F_x of network chains which are x units in length. It has been already indicated that for full elastic effectiveness $x \geq \mu$, where μ is the critical chain length. Those network chains shorter than the critical length, μ, would be effective to varying extents depending upon their length. Equation (6) therefore overestimates the fractional residual network chains, N(t)/N(0). An approximate correction for Eq. (6) would be to change the lower limit of the integral to μ, and to include an additional constant ϵ in the equation so that the condition

$$\int_{\mu}^{\infty} F_x \epsilon \, dx = 1 \tag{7}$$

is satisfied. The value of the constant ϵ can be obtained by substituting for F_x in the above equation from Eq. (4). The effect of these modifications on the form of the network chain-length distribution is illustrated in Fig. 3. Such modification of the chain-length distribution is justified only if the probability of scissions occurring in the short chains ($x < \mu$) is negligible. This is a reasonable assumption at low levels of scission as the total fraction of sites of scission associated with the short chains would be very much smaller than that associated with the other network chains. Equation (6) rewritten in the modified form is

$$\frac{N[t]}{N[0]} = \int_{\mu}^{\infty} \ell^{-1} \exp(-x/\ell) \exp(-\mu/\ell) \exp(-xc/\ell) \, dx \tag{8}$$

$$= (1 + c)^{-1} \exp(-\mu c/\ell) \tag{9}$$

The main weakness of such a simple modification is that all the network chains shorter than the critical length are considered completely ineffective. The more desirable correction would be one which would recognize the partial effectiveness of the network chains which are shorter than, but close to, the critical network chain length.

The weighting of the various fractions of network chains, F_x, with a suitable factor in order to account for partially effective network chains is required. Such a weighted network chain-length distribution would have a well-defined maximum at $x = \mu$ and would be similar in form to Eq. (4) for values of $x > \mu$. The weighted distribution, then, would represent a functional model for the network and would

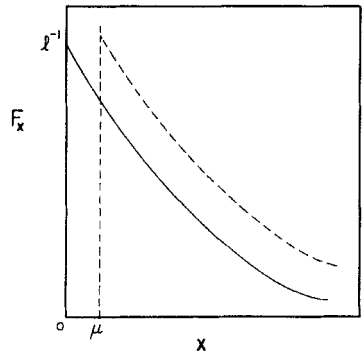

FIG. 3. The effect of replacing Eq. (6) by Eq. (8) upon the theoretical network chain-length distribution of a network where the cross-links are randomly distributed.

be quite different in form from the actual network chain-length distribution in the network. A suitable function to be used for this purpose is the gamma distribution function:

$$*F_x = \frac{\beta^{-(\alpha+1)}}{\Gamma(\alpha+1)} x^{\alpha} \exp(-x/\ell) \tag{10}$$

where α and β are constants. The average network chain length obtained from the above expression (by considering the integral of $x*F_x$ over all possible values of x) is $\ell = \beta(\alpha + 1)$. The maximum value of the function lies at $x = \alpha\beta$, when $x = \mu$. Figure 4 shows the form of $*F_x$ for two values each of α and β. Equation (10) may be written in terms of the average network chain length as

$$*F_x = \frac{\beta^{-\ell/\beta}}{\Gamma(\ell/\beta)} x \frac{(\ell - 1)}{\beta} \exp(-x/\beta) \tag{11}$$

The constant β may be shown to be equal to $(\ell - \mu)$, the difference between the average network chain length and the critical network chain length. Equation (4) of Berry et al. [3] is obtained as a special case of the above equation by setting the critical chain length, μ, at zero.

Consider q cuts being introduced into a network having N[0] chains, whose chain lengths are distributed in accordance with Eq. (11). From Eq. (5), the probability of a network chain which is x units long being

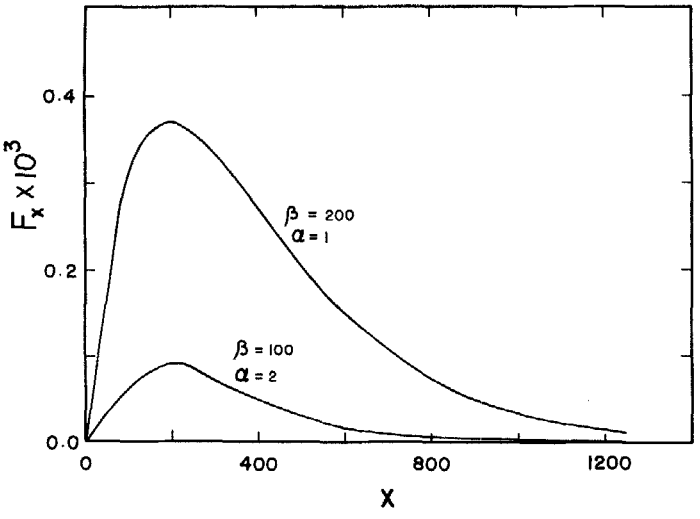

FIG. 4. The form of the modified gamma distribution function (i.e., Eq. 14).

uncut is exp (-xc/ℓ), where c = q/N[0]. The fraction of uncut chains of all lengths may then be obtained by integrating the multiple of the probability factor and the expression in Eq. (11) over all the possible values of x:

$$\frac{N[t]}{N[0]} = \int_0^\infty x^{-\left(\frac{\ell}{\beta} - 1\right)} \exp(-x/\beta) \exp(-xc/\ell)\, dx \qquad (12)$$

This yields

$$N[t]/N[0] = (1 + \beta c/\ell)^{-\ell/\beta} \qquad (13)$$

This final expression is not very different in form from that obtained by Berry et al. [3], given earlier. For values of μ such that $0 < \mu < \ell$, the values of N[t]/N[0] obtained using Eq. (13) are lower than that obtained when Eq. (6) is used to calculate the same. The difference in the value of N[t]/N[0] obtained by the two different equations (Eqs. 6 and 13) may be regarded as the error involved in not taking into account the existence of shorter network chains in the network. This error can be expressed as a fraction E as follows:

$$E = 1 - (1 + \beta c/\ell)^{-\ell/\beta}(1 + c) \qquad (14)$$

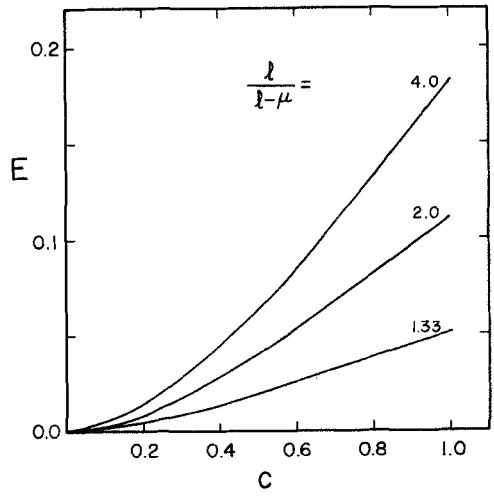

FIG. 5. The dependence of the relative error, E, upon the extent of scission (i.e., the average number of scissions per network chain).

Figure 5 shows several plots of E versus c for different values of $\ell/(\ell - \mu)$.

The relative error E is seen to be small for low values of c (i.e., for results relating to low extents of scission). At high values of c the error might be significant. Nevertheless, at such high extents of scission other errors inherent to the technique of chemical stress relaxation also need to be considered. These latter errors are of comparable magnitude and are very difficult to correct for. (For instance, the effects of concurrent cross-linking might influence the measurement of force in the extended test piece. This effect is referred to as the breakdown of the "two-network hypothesis" [2].) Hence for most practical purposes the error as calculated by the present equation would be very small.

It is interesting to compare the present Eq. (13) with the comparable equations by Tobolsky [2] and by Berry et al. [3]. Figure 6 shows such a comparison. Equation (13) predicts values of f(t)/f(o) which are intermediate between those predicted by the other two equations. Unfortunately, it is as yet not possible to compare the plot in Fig. 6 with experimental results. Such an experiment requires a reliable independent technique for determination of the average number of scissions suffered by a network chain in a test-piece which has been aged. Such a technique sensitive enough for the purpose has yet to be developed.

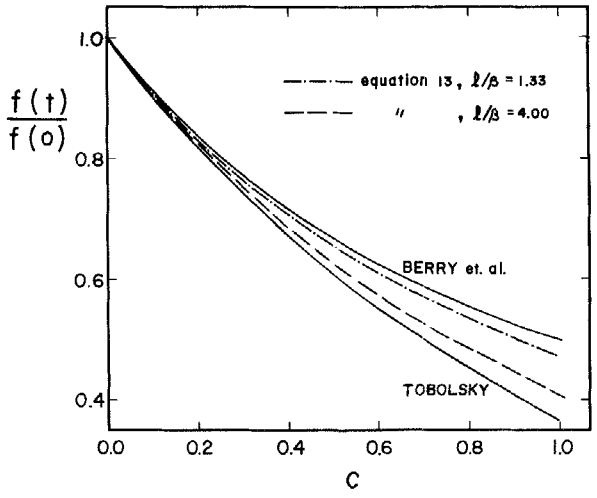

FIG. 6. A comparison of the variation of the fractional residual stress, f[t]/f[0], with the average number of scissions per network chain, c, as predicted by different theoretical treatments.

CONCLUSIONS

The suggested model for the network chain length distribution (in a network where the cross-links are randomly distributed) assumes the eleastic effectiveness of a network chain to depend upon its chain length relative to a critical value of the chain length. Use of the model yields a simple expression for the residual fractional stress in an extended network as a function of the extent of scission. This expression predicts values of f(t)/f(0) which are intermediate between those predicted by the two existing equations for a given value of the average number of cuts per network chain.

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