Elastically Ineffective Polymer Chains in Rubbers

Eugene Helfand* and Alan E. Tonelli

Bell Laboratories, Murray Hill, New Jersey 07974. Received July 1, 1974

ABSTRACT: Chain ends and certain intramolecular loops in a rubber are not elastically effective, because they are tied to the network at only one point. An estimate is made of the fraction of the polymer contained in such defect portions of the rubber. Also some minor improvements are made on our previous calculation of the number of cross-links which close elastically ineffective loops.

In a rubber, cross-links tie together macromolecules into a network, resulting in a group of chains which bear the stress (*i.e.*, have increased free energy) when the network is strained. There occur in the network two types of defects. By this we mean parts of polymer chains which are capable of relaxing when strained and so do not contribute to equilibrium elasticity. One example, chain ends (*cf.* Figure 1), was first discussed by Flory[1] in 1944. In that paper he alluded to another type of defect, intramolecular loops (Figure 2). Both end and loop defects are elastically ineffective by virtue of being tied to the network by only one cross-link (the sol has no links to the network). In Figure 3 we see that some intramolecular loops can be elastically effective, viz., those loops which have another *elastically effective* cross-link along their length. We have not been completely rigorous about such pairs of cross-links, but we believe our estimates to be very good in most cases.

In our previous report[2] an estimate was provided of the fraction of cross-links which closed elastically ineffective loops. The present calculation is aimed at determining the fraction of polymer contained in these loops. Results are also presented for the fraction of polymer in chain ends. In this paper, too, the effect of chain ends is treated in the manner of Scanlan[3] rather than Flory.[1]

The earlier work contained an indication that short loops make an important contribution to the total number of elastically ineffective loops which form. This can be attributed to the fact that short polymer chains have a greater probability of returning to the neighborhood of the origin and also that longer chains have an increased chance of containing elastically effective cross-links along their length. The contribution of longer loops we shall find not to be negligible, however.

To summarize the results in general terms, let us say: (i) the number of cross-links closing elastically ineffective intramolecular loops is a small but nonnegligible fraction for dry state curing and quite a large fraction for curing in a 10% rubber solution; (ii) the effect of this wastage of cross-links is most notable in the amount of polymer contained in chain ends; and (iii) the fraction of polymer contained in the loops is quite small except for the case of solution curing.

We have previously[2] speculated that the elastically ineffective portion of the polymer acts like a diluent in decreasing the Mooney–Rivlin deviations from ideal elastic behavior, even when all solvent has been removed. These calculations make clear how much unstrained rubber is present to serve in this manner.

Theory

The basic concepts for our calculation were developed in the previous paper.[2] We present here a review, into which is incorporated some modification of the way we handle peripheral matters like end corrections.

The virgin rubber will be assumed to consist of N primary macromolecules per unit volume, each with degree of polymerization n, resulting in a density of $\rho = Nn$ repeat units per unit volume. Of these units the density involved in cross-links is ν (*i.e.*, the density of cross-links is $\tfrac{1}{2}\nu$), or the fraction cross-linked is $\alpha = \nu/\rho$.

A fraction g of the cross-links form intramolecular loops. The remaining portion $(1 - g)$ tie the network together, but a fraction of these, s, are sterile. Sterile cross-links join a given chain to another chain which has no other connection to the gel. The formula for s is

$$s = \begin{cases} \exp[-\alpha(1 - g)n(1 - s)] & \alpha(1 - g)n > 1 \\ 1 & \text{otherwise} \end{cases} \quad (1)$$

This equation is essentially due to Flory,[4] except that by including $(1 - g)$ we recognize the fact that intramolecular cross-links cannot contribute to gelation (we have neglected multichain loops).

Not all of the intramolecular cross-links are elastically ineffective, as explained in the introductory section. Some are rendered functional by having another effective cross-link along the loop (Figure 3). We will say that a fraction f of the cross-links close elastically ineffective loops. It was this fraction, f, which was calculated in the previous paper.[2]

In total, the fraction q of units involved in elastically effective cross-links is the sum of: (i) the units with nonsterile intermolecular cross-links, and (ii) the units with intramolecular cross-links that are not elastically ineffective

$$q = \alpha(1 - g)(1 - s) + \alpha(g - f) \quad (2)$$

Let us consider that a cross-link can occur between a unit located at what we will designate the origin and another unit a distance L away (Figure 4). L is a characteristic of the type of cross-linking bridge used; we present results below for $L = 6$ Å.

The key to the quantitative theory is the consideration of several densities in a volume element δV which is a distance L from the unit at the origin. The density in δV of monomer units belonging to the same primary molecules as the one at the origin we term ρ_1 (Figures 4b and 4c). There is a smaller density, ρ_2, of units in δV which are not only part of the same macromolecule as the unit at the origin but also have no intervening elastically effective cross-links along the chain (Figure 4c). The total density in δV (Figures 4a, 4b, and 4c), which we call ρ_3, is greater than ρ, by virtue of the units which are part of the molecule passing through the origin. An estimate for ρ_3, which neglects excluded volume effects except for not allowing densities greater than the density ρ_0 of the undiluted polymer, is

$$\rho_3 = \begin{cases} \rho + \rho_1 & \text{when } \rho + \rho_1 < \rho_0 \\ \rho_0 & \text{otherwise} \end{cases} \quad (3)$$

The fraction of cross-links which close intramolecular loops is
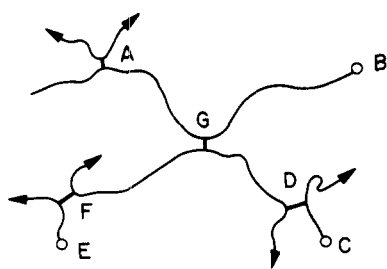
$$g \approx \rho_1/\rho_3 \quad (4)$$

Figure 1. Part of a network. Free ends at B, C, and E produce chain-end defects BG, CD, and EF. Arrows indicate chains which are further connected to the gel.
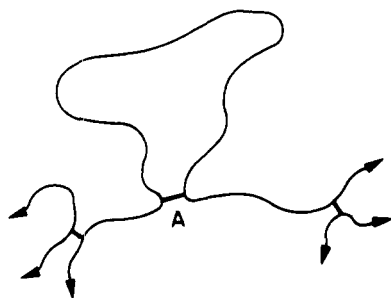

Figure 2. An intramolecular cross-link at A producing an elastically ineffective loop.

while the fraction which close elastically ineffective loops is

$$f = \rho_2/\rho_3 \tag{5}$$

Prominent in the calculation of ρ_1 and ρ_2 is the function $W(L,k)$, the probability density that two monomer units which are k units apart on the same molecule are a distance L apart in space. We will not repeat details of the determination of $W(L,k)^2$ but only point out that for long chains it approaches the well-known Gaussian. For smaller k, 5 to 25, a fourth moment correction to the Gaussian was employed. However, the chains up to four monomer units in length played an important role, so their statistics were evaluated by enumeration of all conformations using a rotational isomeric state model.

In terms of $W(L,k)$, ρ_1 is given by

$$\rho_1 = 2\sum_{k=1}^{n}[1 - (k/n)]W(L, k) \tag{6}$$

The multiplier $[1 - (k/n)]$ is an end correction. To calculate ρ_2, we must include in the summand a factor representing the probability that none of the bonds of the loop are effectively cross-linked to the network; so

$$\rho_2 = 2\sum_{k=1}^{n}[1 -(k/n)]W(L, k)(1 - q)^{k-1} \tag{7}$$

The average length (in repeat units) of an elastically ineffective loop is

$$a_L = \frac{2}{\rho_2}\sum_{k=1}^{n}k[1 - (k/n)]W(L, k)(1 - q)^{k-1} \tag{8}$$

and the fraction of rubber in such loops is approximately

$$F_L = \tfrac{1}{2}\alpha f a_L \tag{9}$$

(loops on loops are double-counted so F_L is a slight overestimate).

In ref 2 we document the case that short loops, let us say ten or less units, make the major contribution to ρ_1 and ρ_2.
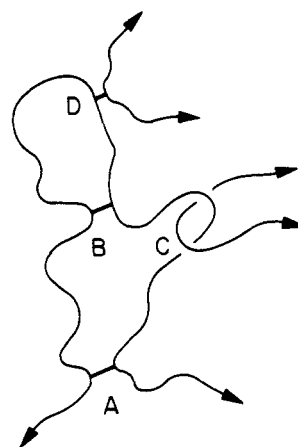

Figure 3. Intramolecular loops rendered elastically effective by virtue of elastically effective connection to the gel at D and entanglement at C.
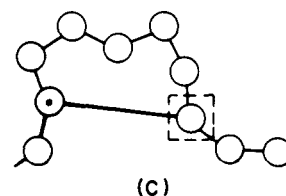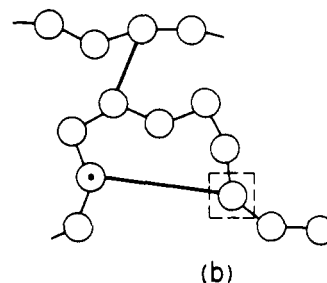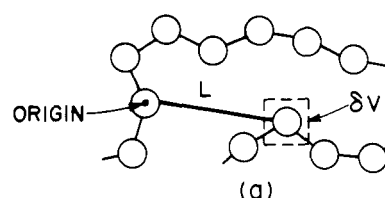

Figure 4. Cross-link between a unit at the origin and a unit in a volume element δV a distance L away: (a) intermolecular, (b) elastically effective intramolecular loop, (c) elastically ineffective intramolecular.

However, the added factor of k in eq 8 for a_L has a profound effect in shifting weight to longer loops. For large k, $W(L,k)$ goes like $k^{-3/2}$; hence a sum like

$$\sum_{k=1}^{\infty}kW(k, L)$$

does not even converge. The factor $(1 -q)^k = \exp[-k/|\,1/\log(1 - q)|]$ provides convergence in eq 8. It effectively cuts off the sum with a characteristic loop length of $|\,1/\log(1 - q)|$; so large loops make a contribution dependent on q.

This is an appropriate point to discuss the effects of entanglements. We have noted[2] that it is difficult to entangle the smaller loops. However, the very large loops have a greater chance of being entangled with the network. To the degree to which entanglements act as elastically effective cross-links, they will remove some of the intramolecular

<div align="center">

Table I
Measures of Elastically Ineffect Loops and Ends
f,[a] a_L,[b] F_L,[c] F_E,[d] and F_T[e] as Functions of α' and φ_r[g]

</div>

φ_r	α, %	f	a_L	F_L	F_E	F_T
1.0	0.375	0.266	26.7	0.013	0.646	0.659
	0.500	0.260	23.9	0.015	0.512	0.528
	0.625	0.254	21.8	0.017	0.419	0.436
	0.750	0.249	20.1	0.019	0.351	0.370
	0.875	0.244	18.8	0.020	0.301	0.321
	1.000	0.240	17.7	0.021	0.263	0.284
	1.125	0.236	16.8	0.022	0.233	0.255
	1.250	0.233	15.9	0.023	0.208	0.232
	1.375	0.229	15.2	0.024	0.189	0.213
	1.500	0.226	14.6	0.025	0.172	0.197
	1.625	0.223	14.0	0.025	0.158	0.184
	1.750	0.220	13.5	0.026	0.147	0.173
	1.875	0.217	13.0	0.027	0.136	0.163
	2.000	0.214	12.6	0.027	0.127	0.154
0.5	0.375	0.314	27.9	0.018	0.695	0.713
	0.500	0.333	24.9	0.021	0.557	0.578
	0.625	0.325	22.7	0.023	0.458	0.481
	0.750	0.319	21.0	0.025	0.385	0.410
	0.875	0.313	19.6	0.027	0.330	0.357
	1.000	0.308	18.4	0.028	0.288	0.317
	1.125	0.303	17.5	0.030	0.255	0.285
	1.250	0.299	16.6	0.031	0.228	0.259
	1.375	0.295	15.9	0.032	0.206	0.238
	1.500	0.291	15.2	0.033	0.188	0.221
	1.625	0.287	14.6	0.034	0.173	0.207
	1.750	0.283	14.1	0.035	0.159	0.194
	1.875	0.280	13.6	0.036	0.148	0.184
	2.000	0.276	13.1	0.036	0.138	0.174
0.1	0.375			Below gel point		
	0.500	0.726	34.9	0.063	0.898	0.961
	0.625	0.712	31.7	0.070	0.811	0.881
	0.750	0.699	29.2	0.076	0.722	0.798
	0.875	0.689	27.1	0.082	0.641	0.722
	1.000	0.679	25.5	0.086	0.569	0.656
	1.125	0.670	24.0	0.091	0.508	0.599
	1.250	0.662	22.8	0.094	0.455	0.550
	1.375	0.654	21.7	0.097	0.410	0.508
	1.500	0.646	20.7	0.100	0.371	0.472
	1.625	0.639	19.9	0.103	0.338	0.441
	1.750	0.632	19.1	0.105	0.309	0.414
	1.875	0.625	18.4	0.108	0.284	0.391
	2.000	0.619	17.7	0.109	0.262	0.371

[a] f is the fraction of cross-links closing elastically ineffective loops. [b] a_L is the average number of monomer units in an elastically ineffective loop. [c] F_L is the fraction of polymer in elastically ineffective loops. [d] F_E is the fraction of polymer in ends (including sol). [e] F_T is the total fraction of defect polymer. [f] α is the fraction of units involved in cross-links. [g] φ_r is the volume fraction of polymer in the system being cured.

loops from the rolls of the defective. It should be pointed out, however, that under the condition of curing in solution, where intramolecular cross-linking is most severe, entanglements are less likely to form.

Let us next estimate the fraction of the polymer which is contained in elastically ineffective ends. Imagine that we have a system of monodispersed primary molecules with degree of polymerization n'. For the moment assume no intramolecular looping. The fraction of units which contain cross-links to other molecules, which themselves are connected by at least one more cross-link to the gel, we call α'. If a molecule contains no such cross-link [probability $\exp(-\alpha'n')$] or only one such cross-link [probability $\alpha'n'$ $\exp(-\alpha'n')$] it is all elastically ineffective. Going on to chains with two or more effective cross-links, we see that the probability density of cross-links first occurring t_1 units from one end and t_2 units from the other end is

$$\alpha'^2 \exp[-\alpha'(t_1 + t_2)]$$

Thus the average length per molecule of elastically ineffective ends (including the sol) is

$$a_E = \int_0^{n'} dt_1 \int_0^{n'-t_1} dt_2 (t_1 + t_2)\alpha'^2 \exp[-\alpha'(t_1 + t_2)] +$$

$$n'(1 + \alpha'n') \exp(-\alpha'n') =$$

$$(1/\alpha')[2 + (\alpha'n' - 1) \exp(-\alpha'n')] \quad (10)$$

To incorporate the effect of looping into this result we will first take as an effective value of n' the true primary degree of polymerization, n, less the average amount in elastically ineffective loops, nF_L

$$n' = n(1 - F_L) \quad (11)$$

Next we note that either a nonsterile intermolecular cross-link or an intramolecular cross-link which has a nonsterile cross-link along the loop can terminate an end. This leads us to take for α' the quantity q of eq 2.

Results

Explicit calculations have been performed for the rubber *cis*-1,4-polyisoprene (PIP), the same material considered in ref 2. A cross-linking bridge length of 6 Å was assumed; degrees of curing, α, between 0.375 and 2% are examined; and curings in the dry state, and in solution with 0.5 and 0.1 volume fraction of rubber, φ_r, are studied.

As compared with the earlier work, the present paper has: (i) modified the formula for ρ_3 to allow for saturation of the density at that of the bulk rubber, and (ii) treated the chain ends in a manner closer to ideas of Scanlan than of Flory. Therefore new values of f, the fraction of cross-links closing elastically ineffective loops, are reported. As expected, these values differ only slightly from the previous ones, except that the case of a $\varphi_r = 0.1$ solution with $\alpha = 0.00375$ is now below the gel point.

Quantitative results are presented in Table I for a variety of α and φ_r. One can get a feel for these numbers by focusing on a few of the cases. When the PIP is cured dry to an extent of 2%, over 21% of cross-links close elastically ineffective loops. The average loop contains approximately 13 monomer units. This is considerably less than the mean distance of approximately 50 (*i.e.*, $1/\alpha$) monomers between cross-links. Thus, only about 3% of the PIP is contained in these loops. However, as a result of the wastage of cross-links the amount of polymer in elastically ineffective ends is 12.7% rather than the 10% predicted by ignoring intramolecular loops.

The extent of elastically ineffective looping sharply increases when curing is carried out in solution. For example, if the same 2% cure is done in a $\varphi_r = 0.1$ polymer solution then 62% of the cross-links close defect loops. These loops have an average length of about 18 repeat units and constitute 11% of the polymer. Furthermore, 26% of the rubber would be wasted in ends.

One profound effect of intramolecular looping is not reflected in the table. If loops are ignored the gel point is $\alpha = 0.001$. However, in $\varphi_r = 0.1$ solution the gel point is $\alpha = 0.0039$ when intramolecular loops are correctly discounted.

References and Notes

(1) P. J. Flory, *Chem. Rev.*, **35**, 57 (1944).
(2) A. E. Tonelli and E. Helfand, *Macromolecules*, **7**, 59 (1974).
(3) J. Scanlan, *J. Polym Sci.*, **43**, 501 (1960).
(4) P. J. Flory, *J. Amer. Chem. Soc.*, **69**, 30 (1947).