Communications to the Editor

Rubber Elasticity. Flaws in the Theory of Networks

It has recently been claimed[1] that "before any properties of a rubber are seriously discussed in terms of detailed network topology, the presence of elastically ineffective cross-links terminating intramolecular loops must be recognized and dealt with." The implicit charge that the extensive literature on rubber elasticity needs this kind of amendment is not, however, justified; on the contrary, the currently accepted model theory allows for the loop effect to an excellent approximation. The new theory proposed,[1] though interesting in several ways, unfortunately overestimates the effect owing to the use of wrong statistics, both as regards the one-dimensional (graph like) and the three-dimensional (configurational) statistics of a vulcanizate.

(a) Graph-Like State Theory of Elastically Active Network Chains (EANCs). The generalized notion of an EANC introduced by Scanlan[2] and by Case[3] is accepted as the basic tool of "detailed network topology."[4-7] It equally embraces the networks prepared by vulcanization of primary chains, by condensation of small molecules (*e.g.*, phenolformaldehyde[8]), or by any other means, *e.g.*, cross-polymerization.[4] Dobson and Gordon[4] were able to summarize free from approximations and to generalize all the results on special cases published from five different sources[2,3,9-11] in the single equation

$$N_e = [\gamma(1 - v^2) - 2(1 - F_o(v))][\gamma(1 - v)(1 - 2v) + 1 - F_o(v)]/\gamma(1 - v)^2 \qquad (1)$$

by restricting attention to vulcanizates. Here N_e is the number of EANCs per primary chain, and

$$\gamma = \alpha \mathrm{DP_n} \qquad (2)$$

where α is the fraction of repeat units cross-linked and $\mathrm{DP_n}$ the number average DP of the primary chains. Restricting ourselves further to the case of homodisperse primary chains treated,[1] the extinction probability v is the largest positive root of

$$v = (1 - \alpha + \alpha v)^{\mathrm{DP}-1} \qquad (3)$$

and

$$F_o(v) = (1 - \alpha + \alpha v)^{\mathrm{DP}} \qquad (4)$$

Finally, restricting further to the case of *long* primary chains[1] and γ values not extremely close to the gel point (see below), we may put $v \sim F_o(v)$ to obtain

$$N_e = (\gamma(1 + v) - 2)(\gamma(1 - 2v) + 1)/\gamma \qquad (5)$$

From this, the (quite general) asymptotic form[12] for high degrees of cross-linking ($\gamma \gg 1, v \rightarrow 0$)

$$N_e \sim \gamma - 1 \qquad (6)$$

emerges by inspection. This equation was discussed in a general survey of the wastage of cross-links in the proper statistical framework.[12] In a further review,[13] it was recommended that the old concept of a chain-end correction should be buried. It is superseded by the correct and generalized theory based on Scanlan-Case EANCs. Tobolsky's form of the chain-end correction was obtained by writing eq 6 as an exact equality; the older approximation, used as the basis in the work under discussion,[1] reads

$$N_e = \gamma - 2 \qquad (7)$$

At high γ, this introduces an error about equal to the proposed loop correction (Figure 1), and near the gel point a much larger error. No statistical subtleties are involved; eq 6 merely asserts that a chain with (an average of) γ cross-linked units harbors (an average of) $\gamma - 1$ chain segments separating these units (and at high γ almost all these segments are EANCs). The argument[1] that it takes two cross-linked units per primary chain to link the complete system into a ring-free gel is also fine. But the equilibrium modulus is measurable long before all the chains are incorporated into the gel, so that the argument furnishes a bad approximation especially for extrapolation back to low conversions. In particular, the gel point in the (ring-free) cross-linking of homodisperse chains of DP = 1000 occurs at $\gamma \simeq 1.001$ and not at $\gamma = 2$ as stated[1] (*i.e.*, when $\nu = 2N$ in the original notation).

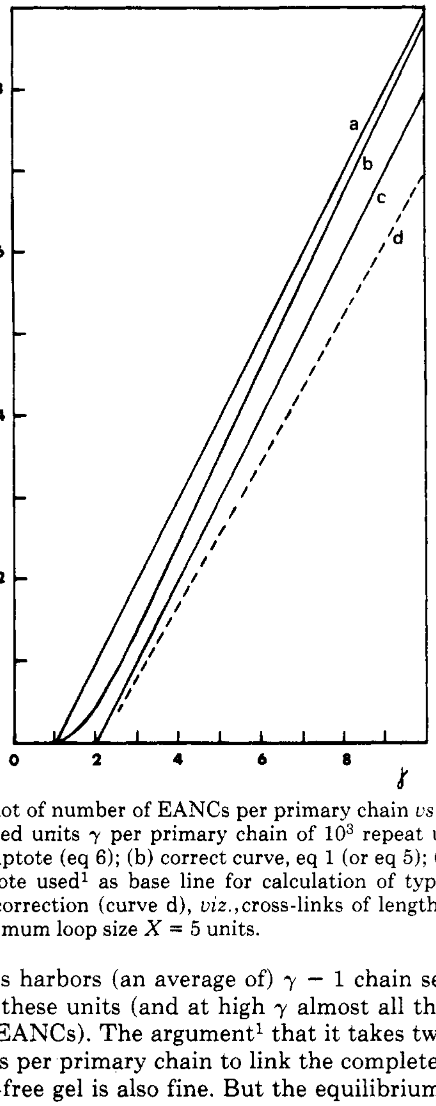

Figure 1. Plot of number of EANCs per primary chain *vs.* number of cross-linked units γ per primary chain of 10^3 repeat units: (a) correct asymptote (eq 6); (b) correct curve, eq 1 (or eq 5); (c) incorrect asymptote used[1] as base line for calculation of typical supposed loop correction (curve d), *viz.*, cross-links of length L = 0.2 nm and minimum loop size X = 5 units.

(b) Three-Dimensional Configurational Statistics. The sort of model described by Tonelli and Helfand,[1] though it works well before the gel point, greatly overestimates the loop effect on rubber elasticity. It has been pointed out,[14] with the aid of a long quotation from Guth and James,[15] that after the gel point the situation is simpler, and the right theory was formulated and verified against experimental data.[14] More extensive experimental verification has been achieved by Ross-Murphy.[16] Briefly, loop formation *within an EANC* proceeds at so slow a rate that in bulk systems, it may be neglected. Gaussian end-vector statistics[1] do not apply, because of the constraints imposed on the branch points at the end of the EANC by the rest of the network (*cf.* James and Guth[15]). Loops formed in the loose material not belonging to an EANC, and surviving in a harmful form during cross-linking up to γ = 10 (*cf.* Figure 1), say, can account for only a tiny fraction of the cross-links introduced up to that stage. In conformity with the treatment of minor disturbances in critical-point phenomena generally (see Fisher and Scesney[17]), the true effect is allowed for[14] by the appropriate rescaling, *i.e.*, replacing γ by γ/γ_c in comparing experiments with plots like b, Figure 1, to an excellent approximation. The recent Faraday discussion on gels did reveal a more general lack of awareness, especially of the Scanlan-Case EANC concept. I propose to review the subject at the forthcoming IUPAC microsymposium on cross-linking and networks in Prague.[18]

References and Notes

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Comments on "Rubber Elasticity. Flaws in the Theory of Networks"

In the accompanying communication[1] Gordon levels two criticisms at our recent work "Elastically Ineffective Cross-links in Rubbers." [2] His first comment is that we have treated chain ends with concepts first employed by Flory,[3] but no longer considered to be the most applicable approach. Scanlan[4] and Case[5] have presented a superior point of view on the elastic activity of cross-links, which Gordon suggests we use. Actually, at the time we first received this comment from Gordon we were about to submit a paper in which, among other things, just such a change had been made, and this work is now published.[6] Chain ends are not central to the counting of elastically ineffective cross-links, except near the gel point. Hence, the modifications of the numerical results we published earlier[2] are slight. We agree, however, that if the free-end correction is to be made at all, it should be made with the theory of Scanlan and Case.

In section b of his communication Gordon claims that in Gordon, Ward, and Whitney (GWW)[7] the correct theory of loop formation in rubbers has been presented. We do not agree that this is the case. (Most of Gordon's work is specific to network formation by condensation reactions of polyfunctional groups, but we are willing to assume that somehow this can be related to rubber vulcanization.)

Our major reservation about GWW is the complete disregard, by fiat, of any correlation between pairs of units which are part of the gel. This includes the case where units are separated by only a few links, a case that we know dominates the loop formation problem. It is not hard to see that this omission of correlation results in no loop formation. However, we do not accept the hypothesis; nor do we regard GWW's four-parameter fit to condensation rates as proof of the approximation as it applies to loop formation. Furthermore, we do not believe that James and Guth[8] felt that such a hypothesis was to be made. While it is true that they pursue its consequence in one section (from which GWW quote), they also consider other, indeed strong, correlation schemes. The major thrust of James and Guth's argument is that the elasticity formula obtained is not overly sensitive to the correlation assumed.

GWW do consider certain loops, *viz.*, those formed in the sol. These are not directly equivalent to any of our elastically ineffective loops. As the functionalities along sol loops join the gel such loops may, in fact probably will, become elastically effective in the sense of the topological theories of rubbers.[9] (By the topological theories we mean those approaches which are based on the number of effective chains in the network, and are independent of the way the cross-links were formed.) Of course, if one adheres strictly to the 1947 James and Guth[8] ideas, it is the condition of a bond at the moment of formation that counts (but in James and Guth[8] all network cross-links, including loops, contribute to the elastic modulus). We do not wish to comment on this disagreement here, but feel free to carry out calculations which are of interest to adherents to the topological school.

We think that some of the kinetic equations of GWW could be adapted to the calculation of elastically ineffective looping (as we define it) by allowing for gel loop formation and by statistically monitoring the subsequent connectivity of those loops to the network. This is not a program we intend to implement at this time.

References and Notes

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Motion of Nitroxide Spin Labels Covalently Attached to Synthetic Polymers

The use of nitroxide spin labels to study motion, environment, conformation, etc., in biological systems is extensive.[1,2] The type of problems involving synthetic polymer systems which can be usefully explored by this technique is not so well established. A few studies on motion in dilute polymer solutions have appeared,[3-10] as well as studies on motion in more concentrated solutions[9,11,12] and also in the pure polymer.[6,9,12-16] In dilute solution spin labels attached to random coil polymers typically undergo rapid motion ($\tau_R \approx 10^{-10}$ sec) which can be analyzed using theory for motionally narrowed spectra.[17] In solid polymers the motion of the spin label may be several orders of magnitude