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The Constant Volume Tube Model of Rubber Elasticity

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Summary

A tube model is presented which provides a surprisingly good description of the simple extension and compression behavior of a cross-linked rubber, while remaining conceptually and mathematically simple.

Introduction

The use of an analogy to the Einstein model of solids to account for the entanglement constraints on a chain in a polymeric solid has been proposed (EDWARDS 1967). The chain is restricted to a tubelike region with a strain invariant, harmonic well potential acting laterally to the center line of the tube. It has been out (de GENNES 1974) that while the Edwards tube is soft, allowing a chain to build up loops extending out of the nominal tube region, it is mathematically equivalent to a hard, impenetrable tube. He also suggested that the tube cross section deforms affinely, rather than remaining constant.

The harmonic potential concept has been applied (EDWARDS 1977) to a network chain, which is a chain having its ends separated and attached to cross-links or junction points. Taking a network chain, a 'primitive path' is defined as the shortest path between the cross-links that does not violate any topological constraints on the chain. The segments of the chain are divided into two populations; those lying along the primitive path and those in the 'surplus population'. The surplus segment population makes 'excursions' by executing a three dimensional random walk. In the walk, one dimension is along the primitive path and two dimensions are orthogonal to the path and subject to the tubelike harmonic potential. Under deformation, the end-to-end separation of the real chain, and therefore the primitive path length, increases. This requires the transfer of chain segments from the surplus population to the path population. The remaining surplus population again executes a random walk while subject to the same harmonic potential, i.e., in the same 'potential pipe', as in the undeformed state. The entropy of deformation of the network chain is given by the difference between the entropy of the surplus population chain in the deformed state and the entropy of the

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surplus population chain in the undeformed state. The model has two parameters: α, which is a measure of the primitive path length relative to the chain contour length and; β, which is a measure of the number of entanglements relative to the number of cross-links in the network. The potential pipe model fails because it makes two incorrect predictions: a catastrophic stress rise in extension and a rapid stress fall in compression on a Mooney-Rivlin type stress-strain plot (GOTTLIEB et al 1981). The extension catastrophe occurs, according to Edwards, not as a result of the finite extensibility of the chain, but as a result of the continuing depletion of the surplus population with increasing extension until the excursions are finally extinguished. The potential pipe model assumes that the tube which confines the surplus population has a strain invariant cross section. Modifying the model so that the tube diameter deforms affinely does not unfortunately, prevent the catastrophic stress rise from occuring.

An alternative tube model, in which the entire network chain is enveloped within a tube and both the chain and the tube deform was recently proposed (GAYLORD 1979) and subsequently modified (MARRUCCI 1981).

The Model

The free energy of confining a Gaussian network chain, having n segments and end-to-end separation l, in either a soft tube (MARRUCCI 1981) or a hard tube (GAYLORD 1979) having cross sectional area a^2, has two terms: The free energy term representing the end-to-end separation of the chain has the usual Gaussian form

$$A_g \propto \frac{l^2}{n} \qquad (1)$$

The free energy term representing the confinement of the chain within the tube is

$$A_c \propto \frac{n}{a^2} \qquad (2)$$

(There is also a free energy term representing the mobility of the chain ends, $A_j \propto \ln a$, which will not be considered, herein.)

Although the chain free energy expressions derived by Gaylord and by Marrucci are identical, their depiction of the tube dimensions and of the network differ. Gaylord's hard tube has a square cross section and is infinitely long. His network is a three-tube network, with each tube aligned along one of the principal directions of strain. Marrucci's soft tube has a circular cross section and extends only to the chain ends, where it is penetrable. His network is comprised of randomly oriented tubes.

Assuming that the network chains deform affinely, Gaylord and Marrucci both find that for simple extension or compression, the chain end separation term gives the classical Gaussian free energy and stress results,

$$A_g(\lambda) \; \alpha \; (\lambda^2 + 2\lambda^{-1}) \tag{3}$$

$$\tau_g \; \alpha \; (\lambda - \lambda^{-2}) \tag{4}$$

Assuming that the tubes deform affinely, as Gaylord does and as Marrucci does in one case, A_c and τ_c for simple extension or compression have the form

$$A_c(\lambda) \; \alpha \; (\lambda^{-2} + 2\lambda) \tag{5}$$

$$\tau_c \; \alpha \; (1 - \lambda^{-3}) \; \alpha \; (\lambda - \lambda^{-2})\cdot(\lambda^{-1}) \tag{6}$$

Marrucci also considers an alternative assumption about the change in the tube dimensions with deformation: the tube length deforms affinely while the tube cross section remains circular and deforms in such a way that the tube volume remains constant; i.e., $(a^2 l)$ is strain invariant. In this case, A_c and τ_c for simple extension or compression, go as

$$A_c(\lambda) \; \alpha \; (\lambda^2 + 2\lambda^{-1})^{1/2} \tag{7}$$

$$\tau_c \; \alpha \; (\lambda^2 + 2\lambda^{-1})^{-1/2} \cdot (\lambda - \lambda^{-2}) \tag{8}$$

We have made a Mooney-Rivlin type stress-strain plot of the sum of eqs.(4) and (8), adjusting the coefficients of these terms so as to fit the theoretical curve to the experimental data at $\lambda = 1$ and 2. The curve is shown in the accompanying figure. The Marrucci curve shows the very undesireable feature of rapidly dropping with increasing λ^{-1} in compression, in much the same way as the Edwards model curve (we note that a corresponding plot of the sum of eqs.(4) and (6) rises with increasing λ^{-1} in compression, which is also unsatisfactory). In analyzing the Marrucci derivation, we have found that he uses, $\langle l \rangle = \langle l^2 \rangle^{1/2}$. This relationship is mathematically unsound.

We have incorporated the constant tube volume assumption into the Gaylord three-hard tube model because the model is a simple but satisfactory way to represent the network and its use enables us to avoid having to make any mathematical assumptions and approximations of the type used by Marrucci. We redefine the hard tube so that it extends only to the ends of the chain and we assume that in deformation, the tube length deforms affinely while the tube cross section remains square and changes so as to conserve the volume of the tube. The resulting A_c and τ_c

expressions for simple extension or compression are

$$A_c(\lambda) \;\alpha\; (\lambda + 2\lambda^{-1/2}) \tag{9}$$

$$\tau_c \;\alpha\; (1 - \lambda^{-3/2}) \tag{10}$$

In the accompanying figure, we have graphed the sum of eqs.(4) and (10) in a Mooney-Rivlin type stress-strain plot, adjusting the coefficients of these terms so as to fit the theoretical curve to the experimental data at $\lambda = 1$ and 2. The Gaylord curve is clearly a great improvement over the Marrucci curve.

It must be noted that the constant tube volume assumption carries with it, the assumption that defect chains, i.e., loops, dangling ends and sol chains, do not contribute to the equilibrium elastic response of a rubber, if after the imposition of a strain, the end-to-end separations of these chains eventually relax back to their unperturbed values. This view contrasts with our previous stance on the matter (GAYLORD 1979), which was based on the postulate that the tube dimensions vary with the macroscopic deformation but are independent of the dimensions of the chain which the tube encompasses. The postulate, in turn, arose from the idea that there is no constraint release mechanism operating in a cross-linked network. This issue merits further consideration.

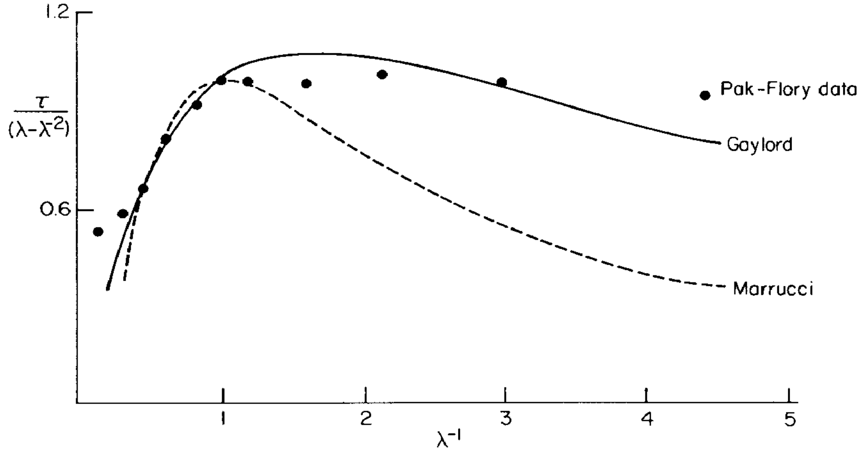

Figure 1. Mooney-Rivlin stress-strain curves predicted by tube models which employ the constant tube volume assumption

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