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The Equilibrium and Non-Equilibrium Elastic Behavior of Cross-Linked Polymer Networks

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Summary

The tube model of rubber elasticity (GAYLORD 1979, MARRUCCI 1981, GAYLORD 1982) is developed in detail and is shown to be able to describe both the equilibrium stress-strain, shear modulus and swelling behavior and the non-equilibrium elastic behavior of cross-linked polymer networks.

Introduction

A simple heuristic construct for treating the entanglement constraints on a chain in a network is to confine the chain in a hard tube which extends to the ends of the chain and which has a square cross section. Using this, a primitive model of rubber elasticity can be developed, using a three-tube network with each tube aligned along one of the principal directions of strain and assuming that during deformation, the end-to-end chain separation and the tube length change affinely while the tube cross section remains square and changes so as to conserve the volume of the tube. In this paper, we will develop this naive model in detail and examine its predicted equilibrium stress-strain, shear modulus, and swelling behaviors. We will also show how the non-equilibrium, time dependent elastic response of the model can be calculated.

The Equilibrium Elastic Response of the Model

The free energy expression for a network chain which has n segments, each of length b, and end-to-end separation l, and which is confined within a retangular hard tube of length l and cross sectional dimensions a_1, a_2 is (GAYLORD 1979)

$$\frac{A}{kT} = \frac{3l^2}{2nb^2} + \frac{\pi^2 nb^2}{6}\left[\frac{1}{a_1^2} + \frac{1}{a_2^2}\right] + \ln a_1 a_2 + \text{constant} \qquad (1)$$

(We note that eq.(1) has the same form as the free energy expression for a chain in a soft tube endowed with a harmonic potential (MARRUCCI 1981)).
For the case of a tube with a square cross section, eq.(1) becomes

$$\frac{A}{kT} = \frac{3l^2}{2nb^2} + \frac{\pi^2 nb^2}{3a^2} + 2\ln a \qquad (2)$$

We now construct a three-tube network model, taking one tube along each of the principal directions of strain (DiMARZIO 1968, GAYLORD 1979). We assume that in a constant volume deformation, the tube length and the end-to-end chain separation change affinely while the tube cross section remains square and changes so as to conserve the tube volume, i.e., that $a^2 l = a_i^2 l_i$ (MARRUCCI 1981, GAYLORD 1982). For the case of simple extension or compression, the tube oriented parallel to the direction of stretch changes as $l = \lambda l_i$, $a = \lambda^{-1/2} a_i$ while the two tubes oriented perpendicular to the direction of stretch change as $l = \lambda^{-1/2} l_i$, $a = \lambda^{1/4} a_i$.

The total free energy of a perfect network of ξ network chains under simple extension or compression is given, using eq.(2), by

$$\frac{A_{Network}}{kT} = \frac{1}{3}\left[\frac{3l_i^2}{2nb^2}(\lambda^2 + 2\lambda^{-1}) + \frac{\pi^2 nb^2}{3a_i^2}(\lambda + 2\lambda^{-1/2})\right]\xi \qquad (3)$$

The stress-strain expression for the model is calculated, using eq.(3) and $\tau = (\partial A/\partial\lambda)$, to be

$$\frac{\tau}{(\lambda - \lambda^{-2})} = \left[\frac{l_i^2}{nb^2} + \frac{\pi^2 nb^2}{9a_i^2}\cdot\frac{(1 - \lambda^{-3/2})}{(\lambda - \lambda^{-2})}\right]\xi\, kT \qquad (4)$$

We expect that the cross sectional area of the tube which encompasses a network chain prior to deformation, a_i, is larger than the cross sectional area of the tube surrounding the same chain in the uncross-linked, parent polymer, a_o (MARRUCCI 1981). The ratio of (a_o^2/a_i^2) which we will denote by the parameter r, should be proportional to the 'entanglement trapping factor'. We expect the end-to-end chain separation in the uncross-linked, parent polymer, l_o, to be larger than the end-to-end chain separation in the undeformed network, l_i. The ratio of (l_i^2/l_o^2), which we will denote by the parameter s, should be proportional to the 'front factor'. We can make the following identifications: $n\xi$ is the polymer concentration, ρ; $a_o^2 = (\rho b)^{-1}$ (deGENNES 1974); and $b^3\rho^2 kT$ is the plateau modulus, G_N^o, of the uncross-linked, parent polymer. Overall then, we can rewrite eq.(4) as

$$\frac{\tau}{(\lambda - \lambda^{-2})} = \frac{l_o^2}{nb^2}\, s\, \xi kT + \frac{\pi^2}{9}\, r\, G_N^o\, \frac{(1 - \lambda^{-3/2})}{(\lambda - \lambda^{-2})} \qquad (5)$$

(We note that if we write eq.(5) in the form $\tau/(\lambda - \lambda^{-2}) = \beta_1 + \beta_2 (1 - \lambda^{-3/2})(\lambda - \lambda^{-2})^{-1}$ and make a best fit of

this expression to the experimental extension-compression data of Pak-Flory on polydimethylsiloxane networks and of Rivlin-Saunders on natural rubber networks, using a least-sum-of-squares criterion, we find that $\beta_1 = 0.356$, $\beta_2 = 1.430$ and the correlation coefficient is 0.973 for the Pak-Flory data, while $\beta_1 = 0.681$, $\beta_2 = 2.165$ and the correlation coefficient is 0.899 for the Rivlin-Saunders data (GOTTLIEB 1982)). The shear modulus is calculated using eq.(5) and the relationship $G = \lim_{\lambda \to 1} \tau/(\lambda - \lambda^{-2})$. We obtain

$$G = \frac{l_o^2}{nb^2} s \xi kT + \frac{\pi^2}{18} r G_N^o \qquad (6)$$

(We note that the form of eq.(6), $G = \alpha_1 \xi + \alpha_2 G_N^o$, is in agreement with experiment (GOTTLIEB et al 1981). If we were to use eq.(2) to describe the uncross-linked, parent polymer, minimized that free energy expression with respect to n to obtain the equilibrium segment line density, (n/l_o), and then used the result in eq.(6), we would predict that the shear modulus is proportional to G_N^o and is independent of ξ. (MARRUCCI 1981). The Flory junction fluctuation suppression model of rubber elasticity predicts that G is proportional to ξ and is independent of G_N^o).

The swelling behavior of a network chain in the three-tube model is calculated using the free energy expression in eq.(2) and taking l and a to both vary directly with λ

$$\frac{A}{kT} = \frac{1}{3}\left[\frac{9\, l_o^2}{2nb^2} s \lambda^2 + \frac{\pi^2 nb^2}{a_o^2} r \lambda^{-2} + 6 \ln \lambda\right] \qquad (7)$$

According to eq. (7), each of the ends of a network chain contributes a $\ln\lambda$ term for the junction it is connected to. The total free energy of a perfect network of ξ network chains is therefore

$$\frac{A_{Network}}{kT} = \frac{3 l_o^2 \lambda^2}{2\, nb^2} s \xi + \frac{\pi^2\, nb^2\, \lambda^{-2}}{3\, a_o^2} r \xi + \frac{\xi}{2} \ln \lambda \qquad (8)$$

where we have divided the logarithmic term by four to avoid an overcounting of the junction contribution to the network free energy which arises from the fact that each junction in a perfect network has four chains attached to it.
(Noting that $(\xi/2)$ equals the number of junctions, μ, in a perfect network, the logarithmic term in eq.(8) is the same as the term representing the fluctuation of a junction within the soft tubes surrounding the chains emanating from the junction (MARRUCCI 1981)).
The elastic contribution to the chemical potential of the diluent in an isotropically swollen network, $\lambda \cdot (\bar{\mu} - \bar{\mu}_o)_{el}$, is given by $-1 \cdot \partial(A_{Network})/\partial\lambda$. Maximizing $\lambda \cdot (\bar{\mu} - \bar{\mu}_o)_{el}$ with respect to λ we find

$$\lambda_{max} = \left[\frac{4}{3} \frac{\pi^2 nb^2}{a_o^2} r \frac{\xi}{\mu} \right]^{1/2} \qquad (9)$$

(We note that the prediction that $\lambda \cdot (\bar{\mu} - \bar{\mu}_o)_{el}$ passes through a maximum is in qualitative agreement with experiment (BROTZMAN and EICHINGER 1982)).

The Non-Equilibrium, Elastic Response of the Model

The assumption that the tube cross section changes as a function of the change in the chain length, so as to conserve the tube volume implies that defect chains, i.e., loops, dangling ends and sol chains, do not contribute to the equilibrium elastic response of a cross-linked rubber, if after the imposition of a strain, the end-to-end separations of these defect chains eventually relax back to their unperturbed values. Nonetheless, these defect chains should bear the responsibility for the time-dependent, non-equilibrium elastic response of the network.

We can very simply incorporate time dependence into the tube model by making use of the experimental factorability of time and deformation in polymeric stress behavior (THIRION 1982),

$$\sigma(t,\lambda) = g(\lambda) \cdot f(t) \qquad (10)$$

In the case of a static, step strain deformation, dangling ends and sol chains initially deform in the same manner as network chains. We can therefore calculate $g(\lambda)$ using eq.(5) from the tube model. The quantity $f(t)$ is the fraction of segments in a chain, remaining in the tube at time t. It can be obtained using the first passage time problem analysis (DOI 1980). According to this calculation, $f(t)$ for a sol chain having n segments, is given by the solution to the first passage time problem for a free particle

$$f(t) \sim \exp(-\delta_1 t/n^3) \qquad (11)$$

while $f(t)$ for a dangling end having n segments, is given by the solution to the first passage time problem for a particle in a harmonic potential

$$f(t) \sim \exp[-\delta_2 t/(n^3 e^{\delta 3^n})] \qquad (12)$$

(We note that another method has been developed for calculating $f(t)$ for a dangling end, based on the number of 'tree' conformations of a loop (deGENNES 1975, 1979).

We can also treat the dynamic stress response of these defect chains using a superposition principle, whereby the stress at a given time is obtained by summing the contributions of eq.(10) for the deformation increments which have occurred at previous times (MARRUCCI and HERMANS

1980). This results in the expression

$$\sigma(t,\lambda) = \int_{-\infty}^{t} g\{\lambda(t,t')\} \cdot f'(t - t')dt' \qquad (13)$$

when $f' = - df(t)/dt$ and g is calculated on the basis of the deformation between t' and t.

Conclusion

The tube model (GAYLORD, 1979, MARRUCCI 1981, GAYLORD, 1982) seems to offer a very useful theoretical approach to rubber elasticity. It predicts, at least qualitatively, and in some cases quantitatively, the equilibrium stress-strain, modulus and swelling behavior of cross-linked elastomers. It can also be used to describe the time-dependent, non-equilibrium elastic response of cross-linked elastomers. In view of these accomplishments, we are presently continuing to modify and refine the details of the theoretical model and to examine its experimental implications.

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