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The localization model of rubber elasticity and the stress-strain behavior of a network formed by cross-linking a deformed melt

II. Equibiaxial extension and pure shear

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Summary

The localization model of rubber elasticity is applied to the deformation behavior of networks formed by cross-linking melts in various states of strain, including equibiaxial extension and pure shear.

Introduction

In the first paper of this series (1), the localization model of rubber elasticity (2) was applied to the data of Batsberg et al. (3) in which a melt was (a) uniaxially strained, (b) cross-linked in the strained state, (c) released from its stretched state and, finally (d) uniaxially deformed in various directions. The observed anisotropic elastic response was in good qualitative agreement with the theoretical predictions. In this paper, the localization model is applied to the data of Hvidt et al. (4) for experiments similar to that described above, but with initial biaxial extension and pure shear deformations of the melt.

Localization Model Equations for the Hvidt Data

The concepts underlying the localization model have been fully described elsewhere (5). In applying the localization model to the experimental systems under consideration here, the deformation of the localization contribution to the free energy is taken relative to the unstrained melt state and the deformation of the connectivity contribution is taken relative to the strained state at which cross-linking occurs. The total elastic free energy expression is thus (1):

$$\Delta F = A \sum_{i=x,y,z} [\lambda_{i,2}^{2} - 1] + B \sum_{i=x,y,z} [\lambda_{i,1}^{-2\beta} - 1] \tag{1}$$

where $\lambda_{i,1}$ is the extension ratio in the ith direction, relative to the undeformed, uncross-linked state and $\lambda_{i,2}$ is the extension ratio in the ith direction relative to the state of strain at which cross-linking occurred. The parameter β may be taken to be adjustable, but we will use the value of β = -1/2 as determined in the space filling tube version of the localization model (2).

Equibiaxial Extension Deformation

The state of ease, λ_s, that results from releasing the network formed by cross-linking the equibiaxially strained melt at λ_o, is determined by taking $\partial F/\partial \lambda_s = 0$ in equation 1 and using

$$\lambda_{x,2} = \lambda_{y,2} = \frac{\lambda_s}{\lambda_o} \quad , \quad \lambda_{z,2} = (\lambda_{x,2})^{-2}$$

$$\lambda_{x,1} = \lambda_{y,1} = \lambda_s \quad , \quad \lambda_{z,1} = (\lambda_{x,1})^{-2}$$

This yields

$$0 = \lambda_o^{6} - \lambda_s^{6} - \frac{\lambda_o^{2\beta}\lambda_s^{4}}{P}(\lambda_s^{4\beta} - \lambda_s^{-2\beta}) \tag{2}$$

where P = A/B.

The stress-strain behavior of the sample relative to its state of ease can now be calculated using equation 1. We consider two cases:

a) Equibiaxial extension. In this case

$$\lambda_{x,2} = \lambda_{y,2} = \frac{\lambda_s}{\lambda_o}\lambda \quad , \quad \lambda_{z,2} = \left(\frac{\lambda_s}{\lambda_o}\right)^{-2}\lambda^{-2}$$

$$\lambda_{y,1} = \lambda_{y,1} = \lambda_s\lambda \quad , \quad \lambda_{z,1} = (\lambda_s)^{-2}\lambda^{-2}$$

The resulting stress equation is

$$\sigma_{bb} = 4B[P(r^2\lambda - r^{-4}\lambda^{-5}) + \beta(\lambda_s^{4\beta}\lambda^{4\beta-1} - \lambda_s^{-2\beta}\lambda^{-2\beta-1})] \tag{3}$$

where $r = (\lambda_s/\lambda_o)$.

b) Uniaxial elongation along the x-axis in the plane of strain. In this case

$$\lambda_{x,2} = \frac{\lambda_s}{\lambda_o}\lambda \quad , \quad \lambda_{y,2} = \frac{\lambda_s}{\lambda_o}\lambda^{-1/2} \quad , \quad \lambda_{z,2} = (\frac{\lambda_s}{\lambda_o})^{-2}\lambda^{-1/2}$$

$$\lambda_{x,1} = \lambda_s\lambda \quad , \quad \lambda_{y,1} = \lambda_s\lambda^{-1/2} \quad , \quad \lambda_{z,1} = \lambda_s^{-2}\lambda^{-1/2}$$

which yields the stress equation

$$\sigma_{bx} = B\{P[2r^2\lambda - (r^2+r^{-4})\lambda^{-2}] + \beta[(\lambda_s^{-2\beta} + \lambda_s^{4\beta})\lambda^{\beta-1} - 2\lambda_s^{-2\beta}\lambda^{-2\beta-1}]\} \tag{4}$$

<u>Pure Shear Deformation</u>

For pure shear of the melt, cross-linking in the strained state and finally releasing the network to its state of ease, one uses in equation 1

$$\lambda_{x,2} = \frac{\lambda_s}{\lambda_o} \quad , \quad \lambda_{y,2} = 1 \quad , \quad \lambda_{z,2} = (\lambda_{x,2})^{-1}$$

$$\lambda_{x,1} = \lambda_s \quad , \quad \lambda_{y,2} = 1 \quad , \quad \lambda_{z,1} = (\lambda_{x,1})^{-1}$$

The state of ease is then given by

$$0 = \lambda_o^{\,4} - \lambda_s^{\,4} - \frac{\beta \lambda_o^{\,2} \lambda_s^{\,2}}{P}[\lambda_s^{\,2\beta} - \lambda_s^{\,-2\beta}] \tag{5}$$

The stress-strain behavior relative to the state of ease is determined for three deformation cases:

a) Pure shear. Here,

$$\lambda_{x,2} = \frac{\lambda_s}{\lambda_o}\lambda \;, \quad \lambda_{y,2} = 1 \;, \quad \lambda_{z,2} = \left(\frac{\lambda_s}{\lambda_o}\right)^{-1} \lambda^{-1}$$

$$\lambda_{x,1} = \lambda_s \lambda \;, \quad \lambda_{y,1} = 1 \;, \quad \lambda_{z,1} = \lambda_s^{\,-1} \lambda^{-1}$$

giving the stress equation

$$\sigma_{ss} = 2B[P(r^2\lambda - r^{-2}\lambda^{-3}) + \beta(\lambda_s^{\,2\beta}\lambda^{2\beta-1} - \lambda_s^{\,-2\beta}\lambda^{-2\beta-1})] \tag{6}$$

b) Uniaxial elongation along the x axis. Here,

$$\lambda_{x,2} = \frac{\lambda_s}{\lambda_o}\lambda \;, \quad \lambda_{y,2} = \lambda^{-1/2} \;, \quad \lambda_{z,2} = \left(\frac{\lambda_s}{\lambda_o}\right)^{-1} \lambda^{-1/2}$$

$$\lambda_{x,1} = \lambda_s \lambda \;, \quad \lambda_{y,1} = \lambda^{-1/2} \;, \quad \lambda_{z,1} = \lambda_s^{\,-1} \lambda^{-1/2}$$

with the resulting stress equation

$$\sigma_{sx} = B\{P[2r^2\lambda - (r^{-2}+1)\lambda^{-2}] + \beta[(\lambda_s^{\,2\beta}+1)\lambda^{\beta-1} - 2\lambda_s^{\,-2\beta}\lambda^{-2\beta-1}]\} \tag{7}$$

c) Uniaxial elongation along the y axis. In this case

$$\lambda_{x,2} = \frac{\lambda_s}{\lambda_o}\lambda^{-1/2} \quad , \quad \lambda_{y,2} = \lambda \quad , \quad \lambda_{z,2} = \left(\frac{\lambda_s}{\lambda_o}\right)^{-1}\lambda^{-1/2}$$

$$\lambda_{x,1} = \lambda_s \lambda^{-1/2} \quad , \quad \lambda_{y,1} = \lambda \quad , \quad \lambda_{z,1} = \lambda_s^{-1}\lambda^{-1/2}$$

The resulting stress equation is

$$\sigma_{sy} = B\{P[2\lambda - (r^2 + r^{-2})\lambda^{-2}] + \beta[(\lambda_s^{-2\beta} + \lambda_s^{2\beta})\lambda^{\beta-1} - 2\lambda^{-2\beta-1}]\} \tag{8}$$

<u>Comparison of Theory and Experiment</u>

For equibiaxial extension, we used equation 2 with the experimental λ_o = 1.4220, λ_s = 1.0830 values and β = -1/2 to calculate P equal to 0.0698. These values were then used to best-fit equation 3 to the data for equibiaxial extension from the state of ease. B was found to be .6440. Since B should be independent of the direction of strain from the state of ease (1), these λ_o, λ_s, β, P and B value were then used in equation 4 for uniaxial deformation along the x-axis. (An alternative approach is to determine the value of B which best-fits both types of deformation from the state of ease simultaneously. This would provide a somewhat better quantitative fit between theory and experiment but the qualitative features would remain the same). The two theoretical curves are shown with the data in Figure 1.

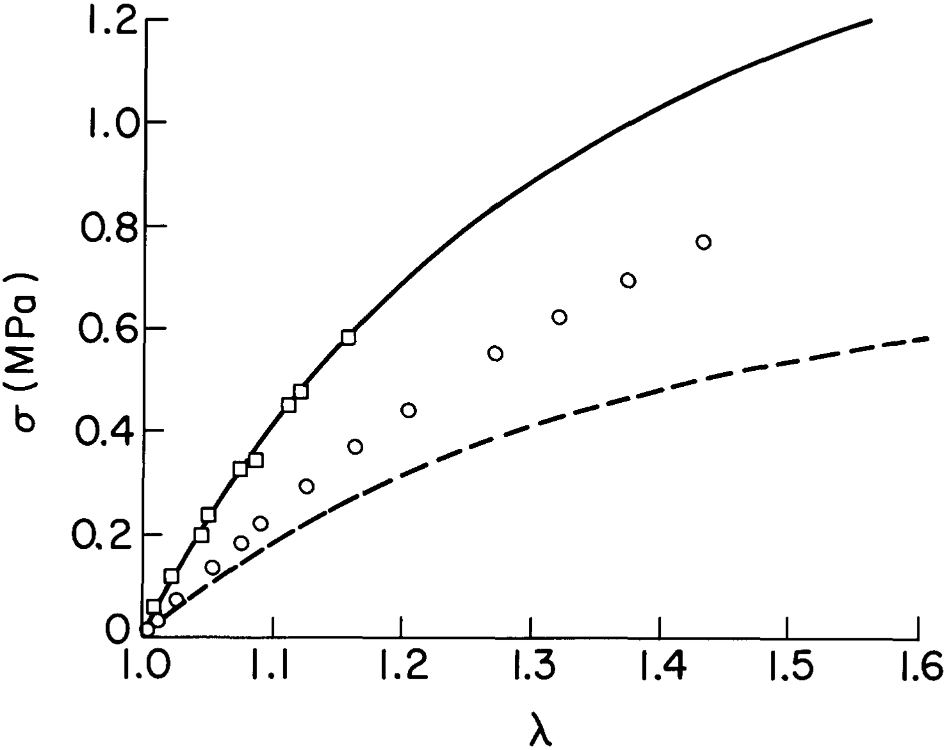

Figure 1. Stress-strain response of deformation from the state of ease: (□) equibiaxial elongation data, (o) x-elongational data, (———) equation 3 for equibiaxial extension, (- - - -) equation 4 for uniaxial elongation along the x-axis.

For pure shear deformation, the experimental values of $\lambda_o = 1.0910$ and $\lambda_s = 1.0200$, were used, along with $\beta = -1/2$, in equation 5 to determine a P value of 0.0677. These values were employed in equation 6, to obtain a best-fit value of B = 1.4232 for pure shear deformation from the state of ease data. These B, P, λ_s, λ_o and β values were then used in equations 7 and 8. The resulting theoretical curves and data are presented in Figure 2.

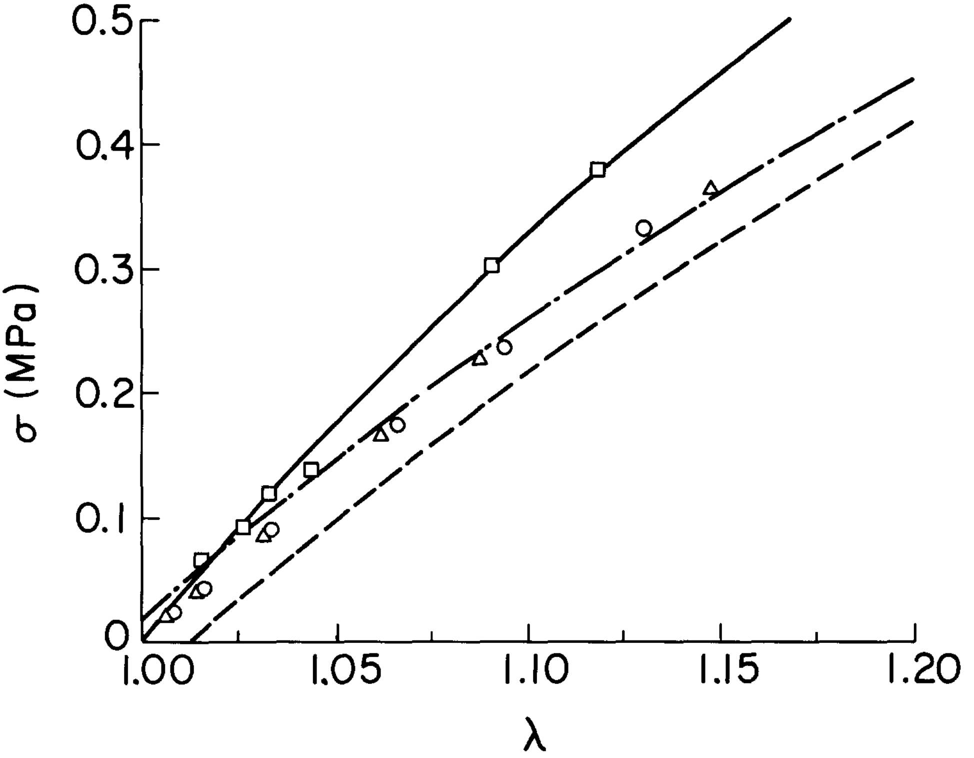

Figure 2. Stress-strain response of deformation from the state of ease: (□) pure shear, (o) x-elongation, (△) y-elongation, (— - —) equation 6 for pure shear, (———) equation 7 for uniaxial deformation along the x-axis, (- - - -) equation 8 for uniaxial deformation along the y-axis.

In Figure 2, several features should be noted: (a) while the deformations along the x and y axes are very similar, other data sets (5) indicate that the y deformation falls below the x deformation, in agreement with the localization theory, (b) the theoretical cross-over at very small strains is a result of the non-zero axial stresses at the state of ease (6) and occurs for any B value used in the theoretical expression. Experimentally both the method of sample preparation and the inherent uncertainty in small strain data may mask this cross-over phenomena (7).

Conclusions

The localization model successfully predicts the qualitative features of the deformation responses found in the experiments of Hvidt et al. (4), as it does for the similar studies of Batsberg et al. (3). In view of the previous success of the localization model in predicting the uniaxial extension-compression behavior of networks formed in the unstrained state (8) and recent successful tests for other deformation conditions, e.g. torsion and swelling [to be published], the model appears to be remarkably useful, especially in view of its conceptual intuitiveness and mathematical simplicity.

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4. Hvidt, S., Kramer, O., Batsberg, W. and Ferry, J., Macromolecules, 13, 933 (1980).
5. Data sets such as sample 13 in ref. 4 display the separation more clearly, but because sample had fewer points with more scatter we used the data set from sample 14.
6. The net force on the network at the state of ease must be zero. Theoretically, for a melt cross-linked in equibiaxial extension this is achieved by individually balancing between the localization term and the connectivity term both the x and y components of the stress. However, for a melt cross-linked in pure shear, these terms do not balance out along the various principal deformation axes, resulting in there being non-zero stress components along the x, y and z directions.
7. Kramer. O., Discussions with T. Twardowski.
8. Higgs, P. and Gaylord, R. J., submitted for publication.

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