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The localization model of rubber elasticity and the deformation of a network formed by cross-linking a strained melt

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Summary

The localization model of rubber elasticity is applied to the deformation behavior of a network formed by cross-linking a strained melt.

Introduction

Recently, Kramer et al. (1,2) made an important study of the effect of interactions between chains on the equilibrium elasticity of cross-linked networks. An uncross-linked melt was isothermally stretched and then held at a constant strain at a temperature above its T_g. The stress was allowed to relax until the plateau region was reached. The sample was then quenched below T_g and cross-linked. It was then reheated to the original temperature and after some time to a still higher temperature to accelerate relaxation. Finally, the sample was cooled back to the original temperature. The final force was found to be within 7% of the value measured in the plateau region prior to cross-linking. Kramer's experiment demonstrates, without using any theoretical model, that the chain interactions existing prior to cross-linking make a substantial contribution to equilibrium network elasticity.

An extension of Kramer's work (3) involved stretching polybutadiene at T_g + 8K, cross-linking it by irradiation at T_g - 25K, reheating the sample to T_g + 8K and then releasing it to allow retraction until the force was zero. The network was subsequently swollen to equilibrium and then dried. Finally, it was deformed in various directions from this state of ease and its stress-strain behavior measured. Below we apply the localization theory of rubber elasticity to Kramer's experiments.

The Localization Model of Rubber Elasticity

Gaylord and Douglas (4) recently developed a simple scaling theory of rubber elasticity which accounts for the minimal features of a cross-linked network: the connectivity of the network chain segments and the 'localization' of chain segments due to interactions (e.g., entanglements, packing) with surrounding network chains. Assuming that the cross-links deform in an affine manner and that the localization parameter deforms in a scaled affine manner, the free energy of deformation expression for a constant volume deformation equals (4),

$$\Delta F_{el} = A \sum_{i=x,y,z} [\lambda_i^2 - 1] + B \sum_{i=x,y,z} [\lambda_i^{-2\beta} - 1] \qquad (1)$$

where $A = (\nu R_o^2/N)$ is proportional to the number of chains in the network and $B = (\nu N/\xi_o^2)$ is proportional to the square of the segment density. Gaylord and Douglas argue that in dense rubbers, β equals - 1/2 if the localization volume of a network chain is constant. This is plausible because localization ultimately derives from the strain invariant hard core volume of the physical chain.

Application of the Localization Model to the Kramer Experiments

In applying the localization theory to Kramer's data, the simplest possible assumption is to use eq. 1 with the deformation of the localization contribution to the free energy taken relative to the unstrained melt state and the deformation of the connectivity contribution taken relative to the strained state at which cross-linking occurs. This gives

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

where $\lambda_{i,1}$ is the extension ratio in the ith direction, relative to the unstrained 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 state of ease, λ_s, that results from releasing the sample after cross-linking at λ_o is calculated by letting $\lambda_{x,2} = (\lambda_s/\lambda_o)$, $\lambda_{y,2} = \lambda_{z,2} = (\lambda_{x,2})^{-1/2}$ and $\lambda_{x,1} = \lambda_s$, $\lambda_{y,1} = \lambda_{z,1} = (\lambda_{x,1})^{-1/2}$ and taking $\partial F_{el}/\partial\lambda_s = 0$ to obtain

$$0 = (\lambda_o^3 - \lambda_s^3) - \beta\lambda_o^2(\lambda_s^{3\beta} - 1)/(P\lambda_s^{2\beta-1}) \qquad (3)$$

where P = (A/B).

Equation 2 can be used to calculate the stress-strain behavior of the sample when it is strained subsequent to being in the state of ease. Two cases will be considered:

(a) Stretching parallel to the original direction of strain. In this case

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

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

The stress then equals

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

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

(b) Stretching perpendicular to the original direction of strain. In this case

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

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

which gives the stress as

$$\sigma_{\perp} = B\{P[2r^{-1}\lambda - (r^2 + r^{-1})\lambda^{-2}] + \beta[(\lambda_s^{\beta} + \lambda_s^{-2\beta})\lambda^{\beta-1} - 2\lambda_s^{\beta}\,\lambda^{-2\beta-1}]\} \qquad (5)$$

Comparison of Theory and Experiment

Using eq. 3, $\beta = -1/2$ and the experimental λ_o, = 1.962, λ_s = 1.247 values, P was determined to be 0.150. Equation 4 with β = -1/2 was then best-fitted to the parallel deformation data, resulting in a B value of 1.648 and a 0.032 standard deviation. While eq. 5 can be independently fitted to the perpendicular deformation data (giving a B value of 1.496 and a 0.016 standard deviation) a molecular model of rubber elasticity should be constitutive and therefore, the B value obtained using eq. 4 was used in eq. 5 with $\beta = -1/2$ to produce the perpendicular deformation curve without any data fitting. Both curves are shown in Figure 1.

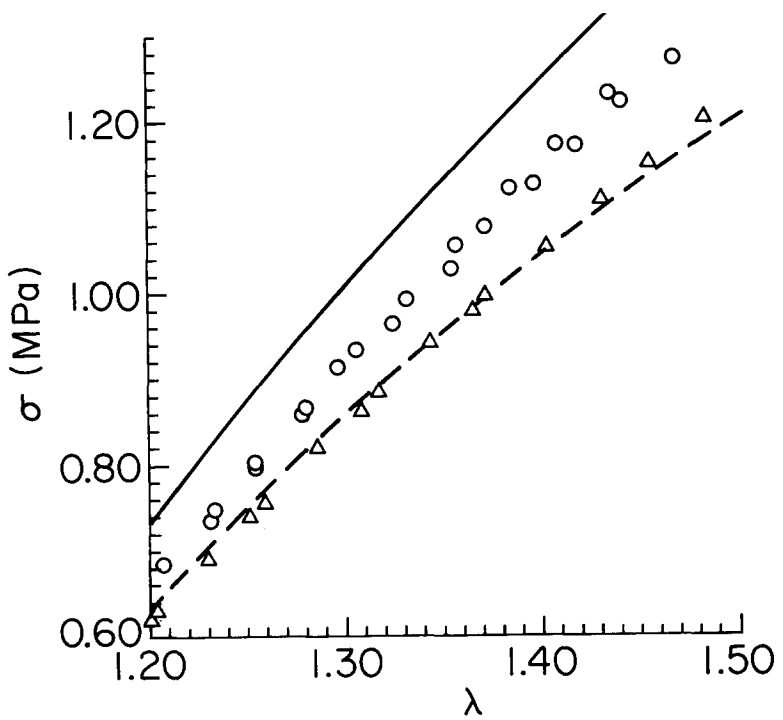

Figure 1. Experimental and theoretical stress-strain plots of parallel and perpendicular stretching of a network cross-linked in the strained state. (o) ⊥ strain data, (Δ) ∥ strain data, (----) $\sigma_{\parallel}$ [eq. 4], (—) $\sigma_{\perp}$ [eq. 5].

In view of our use of the simplified 'two-network' approach (2) in eq. 2, the qualitative agreement between the predicted and observed anisotropic elastic behavior is fairly good (and much better than one obtains using either $\beta = 1$, corresponding to the Mooney-Rivlin equation, or $\beta = -1$, corresponding to the Gaussian composite network). The small value of $P = (A/B)$, indicating that cross-links play a much smaller role than chain interactions, is also in accordance with experimental findings (2).

Conclusion

The localization model of rubber elasticity successfully reproduces the qualitative features of the deformation behavior of a network formed by cross-linking a strained melt. The model has previously performed well in the cases of uniaxial extension-compression and biaxial deformation (4). Other than the case of network swelling behavior, which cannot at the present time be analyzed using any rubber elasticity theory (5), the model's success is quite gratifying, especially in view of its great conceptual and mathematical simplicity. Further testing of the model with experiments on other types of deformation is currently underway (6).

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References

1. Batsberg, W. and Kramer, O., J. Chem. Phys., 74, 6507, 1981.
2. Batsberg, W. and Kramer, O., ACS Symposium Series No. 193, "Elastomers and Rubber Elasticity", 193, 439 (1982).
3. Batsberg, W., Hvidt, S. and Kramer, O., J. Polym. Sci.,Polym. Let., 20, 341 (1982).
4. Gaylord, R. J. and Douglas, J. F., Polymer Bull., 18, 347 (1987).

5. No model of rubber elasticity should be tested using swelling measurements such as the dilation modulus because the Flory theory of network swelling, which is used in conjunction with a model, has fundamental difficulties. For example, experiments indicate that the Flory χ parameter is dependent on both concentration and cross-link density, in conflict with the Flory assumption. Additionally, the Flory assumption that the total free energy is separable into a sum of elastic and mixing contributions has no logical basis and has been theoretically criticized.
6. Preliminary testing with a torsion deformation experiment by G. B. McKenna of the NBS shows reasonable agreement with the localization model prediction.

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