Comment on "Nonaffine Deformation and Elasticity of Polymer Networks"

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In a recent paper in this journal,[1] Rubinstein and Panyukov (R&P) proposed a rubber elasticity model, based on the idea that nonlinear elasticity arises from nonaffine displacement of the "tube" of entanglements confining network chains. They obtained the engineering stress, f, for a uniaxially deformed network as the sum of a phantom and an entangled network contribution

$$f/(\lambda - \lambda^{-2})\ G_c + G_e/(\lambda - \lambda^{1/2} + 1) \qquad (1)$$

in which λ is the stretch ratio, and the quantity $f/(\lambda - \lambda^{-2})$ is the familiar "reduced stress". G_c, the modulus of the phantom network, accounts for the effect of the chemical cross-links, while G_e represents the elastic modulus due to topological interactions. G_e essentially equals the plateau modulus of the corresponding polymer melt.[1]

As pointed out by the authors, eq 1 has a similar form to the Mooney−Rivlin equation[2]

$$f/(\lambda - \lambda^{-2}) = 2C_1 + 2C_2/\lambda \qquad (2)$$

derived by attempting to capture the relevant physics through restrictions on the form of the strain energy function. This phenomenological approach has enjoyed renewed popularity of late.[3−5] For $\lambda > 1$, eqs 1 and 2 behave similarly over moderate extensions. However, the two functions depart for compression, with the R&P model offering some improvement on a principal failing of the Mooney−Rivlin relation, its overestimation of compressive stresses.[2] The parameters of the two models are related as[1]

$$2C_1 = G_c + {}^1\!/_2 G_e; \quad 2C_2 = {}^1\!/_2 G_e \qquad (3)$$

so that C_1 not only represents the chemical network but also includes topological contributions.[6,7] To the extent G_e can be identified with the plateau modulus of the uncured polymer, eq 3 also indicates that C_2 will be independent of cross-link density. While the Mooney−Rivlin plots in Fig. 3 of ref 1 are indeed parallel, more generally, experimental studies have found that C_2 varies with cross-linking.[7−12]

Recognition of the importance of intermolecular interactions in governing chain fluctuations, and hence the elastic energy, originated with Flory's constraint theory of rubber elasticity.[13,14] This model, which addressed how entanglements modify the stress in a strain-dependent manner, has recently been generalized in the continuously constrained chain (CC) model.[15,16] The constraint theories yield expressions in the form

$$f/(\lambda - \lambda^{-2}) = G_c(1 + h(\lambda)) \qquad (4)$$

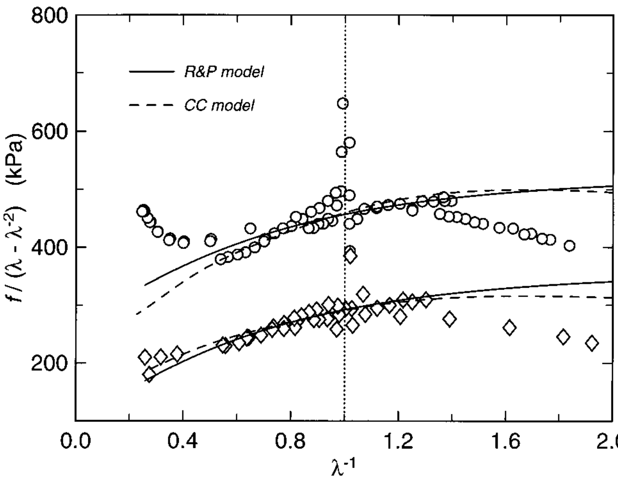

Figure 1. Reduced force vs reciprocal of the stretch ratio for two deproteinized natural rubber networks,[17] along with the least-squares-fits of eq 1 to the extension data (ignoring the upturn in the experimental data for the more cross-linked network, reflecting strain-induced crystallization). The fitting parameters were $G_e = 270$ kPa, and $G_c = 105$ and 187 kPa for the lower and upper curves, respectively. The R−P expression was not capable of describing both tension and compression results. Also shown is the fit of the constrained chain theory.[15,16]

where $h(\lambda)$ is a complicated function of strain describing the severity of the entanglement constraints. Proper assessment of elasticity theories requires comparison to measurements encompassing a range of experimental variables, including different deformation types. Recently, mechanical and optical birefringence data were obtained for cross-linked polyisoprenes deformed in both tension and compression.[17] The constraint theories of elasticity were found to accommodate the stress and birefringence data in tension; however, discrepancies were apparent when both compression and tension data were analyzed together. In fact, the differences between the various constraint models were less than their deviation from experiment. These models overestimate the compressive stress, although the error is not as severe as for the Mooney−Rivlin relation.

In ref 1, it was stated that the R&P model "leads to a stress−strain relation that is in excellent agreement with experiments." However, the model was only compared therein to uniaxial extension data. This is insufficient to demonstrate that eq 1 is a valid constitutive equation. In Figure 1, mechanical equilibrium data are displayed for polyisoprene networks in both uniaxial extension and compression (taken from ref 17). The solid lines in the figure correspond to the R&P model. Since the model could not describe the experimental data over the entire range of strains, eq 1 was fitted to the results for extension, using a least-squares-fit constrained so that G_e is the same for both networks. Hence, the curves depart from the compression results, although the discrepancy for $\lambda < 1$ is less than for the Mooney−Rivlin equation, which would yield a straight line for all λ in Figure 1. The topological parameter, $G_e = 0.19$ kPa, is somewhat smaller than the plateau modulus of polyisoprene, 0.36 ± 0.04 kPa.[18,19] For comparison, we also show (dashed lines) the fit of the CC model to the same data.[17] There are only modest differences between the R&P and CC models.

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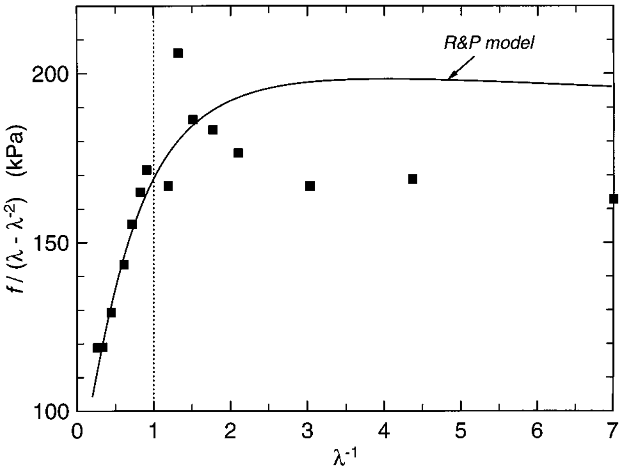

Figure 2. Reduced force vs inverse stretch ratio for sulfur cross-linked natural rubber, taken from ref 21. The solid line is the best-fit of eq 1 to the extension data, which yields G_e = 88 and G_c = 81 kPa.

The experimental data in Figure 1 are noisy, in part due to the nature of the experiments necessary to obtain extension and compression measurements on the same sample but also because of the scatter intrinsic to the ordinate for $\lambda \sim 1$ (some of this may actually be real[20]). The data appear very smooth in a plot of the stress vs the strain. To ensure that the discrepancies between the R&P model and experiment seen in Figure 1 are not artifacts of dubious data, we made the same comparison using another set of published results.[21] These differ from that in ref 17, in that compression was achieved in the former via inflation (biaxial extension). As seen in Figure 2, the scatter around λ equal to unity remains. More relevant herein, the deviation of eq 1 from experimental results for $\lambda < 1$ remains.

In conclusion, the R&P model offers some insights regarding the origin of the elastic behavior of networks. Unfortunately, in accounting for experimental data, the model exhibits shortcomings similar to those of existing elasticity models.

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References and Notes

(1) Rubinstein, M.; Panyukov, S. *Macromolecules* **1997**, *30*, 8036.
(2) Rivlin, R. S. *Rubber Chem. Technol.* **1992**, *65*, G51.
(3) Arruda, E. M.; Przybylo, P. A. *Polym. Eng. Sci.* **1995**, *35*, 395.
(4) Gent, A. N. *Rubber Chem. Technol.* **1996**, *69*, 59.
(5) Boyce, M. C. *Rubber Chem. Technol.* **1996**, *69*, 781.
(6) Carpenter, R. L.; Kramer, O.; Ferry, J. D. *Macromolecules* **1977**, *10*, 117.
(7) Dossin, L. M.; Graessley, W. W. *Macromolecules* **1979**, *12*, 123.
(8) Ciferri, A. *Rheol. Acta* **1973**, *12*, 276.
(9) Mark, J. E. *Rubber Chem. Technol.* **1975**, *48*, 495.
(10) Sanjuan, J.; Llorente, M. A. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 235.
(11) Roland, C. M. *Rubber Chem. Technol.* **1989**, *62*, 863.
(12) Langley, N. R.; Polmanteer, K. E. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1023.
(13) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(14) Flory, P. J.; Erman, B. *Macromolecules* **1982**, *15*, 800.
(15) Kloczkowski, A.; Mark, J. E.; Erman, B. *Macromolecules* **1995**, *28*, 5089.
(16) Kloczkowski, A.; Mark, J. E.; Erman, B. *Comput. Polym. Sci.* **1995**, *5*, 37.
(17) Mott, P. H.; Roland, C. M. *Macromolecules* **1996**, *29*, 6941.
(18) Roland, C. M. *Macromolecules* **1992**, *25*, 7031.
(19) Gotro, J. T.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2767.
(20) McKenna, G. B.; Zappas, L. J. *Polymer* **1983**, *24*, 1502.
(21) Rivlin, R. S.; Saunders: D. W. *Philos. Trans. R. Soc. London, A* **1951**, *243*, 251.

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