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NOTE

The Thermoelasticity of Rubberlike Materials and Related Constitutive Laws

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ABSTRACT

A recently proposed strain-energy-function for elastomeric materials is discussed, together with some recent experiments about the entropic nature of rubberlike elasticity.

Key Words: Elastomers; Thermoelasticity; Strain-energy functions; Inter-chain interactions; Chain dimensions.

INTRODUCTION

Kreitmeier, Böhm, and Göritz have recently proposed a new strain-energy function for elastomers which contains an essential contribution from short-range and strain-dependent van der Waals interactions between network chains.[1] The basic assumption is that there is a deformation-dependent and significant energy contribution to the free

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energy from a (short-range) potential between various repeat units. The strength and the significance of such contributions are questionable, and the assumption made is not generally accepted by the polymer chemistry and physics communities. In an additional complication, the motivation for including such an unusual contribution apparently goes back to strain-calorimetry measurements not available in the open literature. Because of these uncertainties and concerns, the present Note attempts to clarify this issue and some related matters.

One serious issue is that there are "deviations" between the classical entropic origin of the elasticity of rubberlike networks and some relevant experimental studies.[1] The motivation for this conclusion is given in the unpublished 1989 Ph. D. University of Regensburg thesis of R. Grassler, specifically some strain-calorimetry measurements on several elastomers (cited as reference 31 in Ref.[1]). In these thesis results, the mechanical work ΔW and heat ΔQ of deformation of elastomers were measured under isobaric conditions as functions of temperature and strain ratio λ. The internal energy change ΔU was then estimated from the first law of thermodynamics. However, all deviations from the Neo–Hookean part of the uniaxial stress–strain (σ–λ) relation were simply identified with the energetic contribution, f_e, to the total force f (Fig. 21 in Grassler thesis).

EXPERIMENTAL

Treatment of Thermoelastic (Force–Temperature) Data

A careful discussion of the measured ratio f_e/f has to distinguish several cases. Using the thermoelastic concepts of stretched elastomers as a function of temperature at constant length, the following Flory–Hoeve–Ciferri equation is valid.[2–9]

$$\frac{f_e}{f} = 1 - \frac{T}{f}\left(\frac{\partial f}{\partial T}\right)_{p,L} - \frac{\alpha T}{\lambda^3 - 1} \tag{1}$$

where α is the temperature expansion coefficient at constant length. The derivative $(\partial f/\partial T)_{p,L}$ is the temperature coefficient of the force at constant length, which is different from the corresponding temperature coefficient $(\partial f/\partial T)_{p,\lambda}$ at constant deformation ratio λ. Under conditions of constant λ, however, the relative energetic contribution to the total force is

$$\frac{f_e}{f} = 1 - \frac{T}{f}\left(\frac{\partial f}{\partial T}\right)_{p,\lambda} - \frac{\alpha T}{3} \tag{2}$$

This was already discussed in the classic paper of Gee in 1946.[10] The magnitude of the relative force here is influenced by the length of the undeformed sample L_0, and its value depends on temperature T due to intermolecular interactions. Eq. (2) does not contain the term $\sim (\lambda^3 - 1)^{-1}$ that diverges for small stretching ratios (λ → 1). Moreover, this term describes the difference between temperature coefficients at constant length/constant volume and constant length/constant pressure:

$$\left(\frac{\partial f}{\partial T}\right)_{V,L} - \left(\frac{\partial f}{\partial T}\right)_{p,L} = \frac{\alpha f}{\lambda^3 - 1} \qquad (3)$$

Particularly relevant here is a study by Moshin and Treloar,[9] not cited in Ref.[11], on the thermoelastic behavior of polyisobutylene in torsion between 20 and 100°C. They found no significant contributions from intermolecular interactions, and no change of the sign of f_e/f under any conditions.

Alleged Deviations

Somewhat misleading is the claim that "deviations" from the predictions of classical entropy elasticity of elastomers were observed in the thermoelasticity studies of Allen et al.[6,11,12] These unique experiments at constant *volume*, however, were complicated by experimental difficulties in trying to offset changes in volume of the sample by means of extremely large hydrostatic pressures. In any case, in the most recent of these papers, on natural rubber,[6] there was little variation in $f_e/f = 0.18$ over the full range of deformations ($0.88 < \lambda < 1.7$).

We also note that Shen determined a constant $f_e/f = 0.18$ from the temperature coefficients of the shear moduli of natural rubber networks.[13] His method circumvented the difficulty encountered in directly obtaining the relative energy contribution from stress-temperature data, and both constant length and constant stress thermoelastic measurements were used to obtain f_e/f. Furthermore, changes in intermolecular interactions, brought about by the incorporation of diluents, produced no variation in the value of f_e/f.[13] These observations support the conclusion that the energetic part of the force in rubberlike elasticity is indeed attributable to changes in intrachain (conformational) energies of the network chains.

Intermolecular Interactions

The significant intermolecular contribution to the deformation-force relationship in the proposed materials law[1] contradicts previous experimental and theoretical findings on the nature of rubberlike elasticity. Missing from this new analysis is careful consideration of all previous experiments and models in which the relatively small energetic contributions of the force ($f_e/f < \pm 0.2$) are attributed to intra-molecular effects. This is the usual case, where there is a dominance of entropic elasticity, with the only changes in energy being due to changes in conformational energies of the deformed chains as a result of changes in populations or sequential arrangements of rotational isomeric states. This is now done below.

Chain Dimensions and Rotational Isomeric State Theory

In the past, values of f_e/f were estimated from thermoelastic measurements between approximately 20 and 100°C for a multiplicity of polymers, from numerous research groups over a period of several decades. The procedures have been thoroughly described, and results have been extensively tabulated.[2−9,13] In some cases, specifically for experiments carried out at constant volume, the conditions are such that only purely thermodynamic equations are required for interpretation of the experimental data, thus avoiding possible problems with model-based approaches. Even in the other cases, specifically experiments carried out at constant pressure, the only approximation required is that the chains be Gaussian, and these results are found to be in good agreement with those obtained at constant volume.[2−9] These thermoelastic results are also found to be independent of numerous other experimental variables. Specifically, it is very important that f_e/f does not depend on dilution (swelling) down to very low elastomer concentrations (where interchain interactions must be greatly reduced if not entirely eliminated). Furthermore, the values of f_e/f thus obtained are in good agreement with completely independent results obtained by calorimetry, and by viscosity-temperature measurements of unperturbed dimensions $\langle r^2\rangle_o$ through the relationship $d\ln\langle r^2\rangle_o/dT = f_e/fT$.[14] In addition, these results have been quantitatively explained by rotational isomeric state theory. Taken as a whole, the results from thermoelastic studies support the view that the retractive force is primarily intramolecular in origin. It could well be that at very high extensions intermolecular contributions become more important due to strain-induced crystallization or anisotropic averaging of the force field between neighbouring segments.[2] So far, however, there is no way of investigating this region in the absence of crystallization; rubberlike materials which do not crystallize usually fail well before the large extensions at issue are reached.

Potentials in Elasticity Theory

The derivation of the specific form of the interaction term presented in the new analysis[1] is hardly motivated by the Morse potential. There is no doubt that the potential can be used for detailed studies. The essential point, however, is the strength of the potential, which is expressed in its coupling constant, which is not specified at all.[1] In contrast, two fit parameters A and B are introduced. The parameter A stands for the strength of the energetic contribution and should be directly proportional to the coupling constant of the potential, whereas B has its origin in the strength of the attractive (van der Waals) part. There are also some doubts on the derivation and motivation of this contribution. If the network chain Hamiltonian H is modelled by an entropy and energetic term, the corresponding free energy has to be calculated in its “quenched” (non Gibbsian) form. The simplest strategy is then

$$F = -k_B T \langle \log p(\lambda R) \rangle \tag{4}$$

where the average $\langle \ldots \rangle$ is taken on the distribution

$$p(r) \sim \exp\left(-\frac{H(r)}{kT}\right) \tag{5}$$

By use of this standard procedure, a more rational form of the (macroscopic) free energy can be derived. It is then directly seen that the coupling constant of the Morse potential enters as prefactor to the energetic contribution. The question on the magnitude of A remains to be solved. Moreover, it seems that the authors ignore recent detailed theoretical results of Edwards and co-workers, and de Gennes and co-workers. They have shown that in bulk polymers, van der Waals potentials between arbitrary segments of chains determine the density locally, and the incompressibility of the bulk polymer network globally, since their contribution takes the form $\lambda_1\lambda_2\lambda_3$.[15] Only in swollen gels do these terms matter. Only if the Poisson ratio deviates significantly from 1/2, could one argue that these terms have to be revisited. Furthermore, these interactions influence only the compression modulus and not the shear (or elastic) modulus of the network. Physically this becomes clear under various circumstances involving interaction screening. There can be long-range effects in so-called c∗-gels (where c∗ is the critical concentration where polymer coils begin to overlap), and such effects may indeed change stress–strain relationships, but they are irrelevant in dry elastomers. Similar conclusions follow from the inclusion of the van der Waals potential in computer simulations of polymer networks.[16]

Possible Roles of Entanglements

The suggested materials law also ignores the influence of entanglements on the mechanical properties of polymer networks, a subject which has been studied theoretically and experimentally for several decades. The action of entanglements is not simply an additive contribution to the fitting constants in the Neo–Hookian part of the material law, as proposed.[1] Entanglements substantially determine the (constitutive) structure of the strain energy density as a function of the strain variables. The physical connection between entanglements and local deformations of the topological constraints of network chain segments and junctions has been studied using small angle neutron scattering techniques. The findings were in very good agreement with the physical models of entropic rubberlike elasticity and confirm the predicted non-affine deformations on length scales below the entanglement spacing.[17,18] Experiments on block copolymers having different lengths of deuterated sequences showed a crossover from constrained behavior at block dimensions larger than the tube dimensions, to phantom behavior at block dimensions smaller than the tube dimensions.[19] The tube dimensions obtained were in complete agreement with the values obtained from other investigations, for example, stress–strain behavior. Recent work has also yielded macroscopic elastic properties as well as microscopic deformations including structure factors obtained using a (unified) generalised tube model for arbitrary network connectivity.[20]

Additional Relevant Experimental Results

All experimental works about the influence of entanglements on stress–strain properties, swelling behavior, neutron scattering and NMR properties of rubber networks were reviewed recently.[21] The results yield a logically consistent picture of the standard entropic type of rubberlike elasticity, including the effects of finite network chain extensibility. In addition, recent models (e.g., "tube models" or "slip-link models"[22]) also offer the possibility for taking account of other essential details such as effects and mechanisms in connection with deformations of filled elastomers, such as cluster breaking and stress softening.[23]

In one recent paper by Urayama, Kawamura, and Kohjiya detailed experimental comparisons of recent material laws was reported.[24] These authors find, as have many others, that experiments are well accounted for using tube or slip-link models that consider specific contributions from entanglements.

CONCLUSION

It is not unusual for people to reconsider issues that almost everyone else in a field considers well established, as illustrated by another recent example.[25] This is a useful endeavor, but there must be a real possibility of verification relative to other divergent concepts, and the results must demonstrate improvements over the models to be replaced. The proposed elastomeric materials model[1] does not seem to possess a deep physical basis for the various reasons outlined above. It seems more to be another formal phenomenological attempt to describe the stress–strain relationships of elastomers. It would then simply join other such attempts not having a firm statistical–mechanical basis, and be of only limited utility with regard to a molecular understanding of rubberlike elasticity.

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