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Problems in determining the elastic strain energy function for rubber

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ABSTRACT

Lightly crosslinked natural rubber can be stretched by 600% or more, and recovers almost completely. It is often regarded as a model highly elastic material and characterized by a strain energy function to describe its stress–strain behavior under various types of deformation. A number of such functions have been proposed; some of them appear in current finite element programs. They are usually validated by comparison with measured stress–strain relations by Treloar [7] [L.R.G. Treloar, Stress–strain data for vulcanized rubber under various types of deformation, Trans. Faraday Soc. 40 (1944) 59–70] and Jones and Treloar [15] [D.F. Jones, L.R.G. Treloar, The properties of rubber in pure homogeneous strain, J. Phys. D Appl. Phys. 8 (1975) 1285–1304]. But Treloar pointed out that the relations at high strains became markedly irreversible, and he did not assign a strain energy function for strains greater than about 300%. Rivlin's universal relation between torsional stiffness and tensile stress [14] [R.S. Rivlin, Large elastic deformations of isotropic materials. Part V1: further results in the theory of torsion, shear and flexure, Philos. Trans. R. Soc. A 243 (1949) 251–288] is applied here to show that a typical elastic solid cannot be described by any strain energy function at strains greater than about 300%. Elastic strain energy functions for higher strains, or for other rubbery materials, are thus of doubtful value unless evidence for reversibility of stress–strain relations is adduced or the applicability of a strain energy function is demonstrated.

1. Introduction

Lightly crosslinked natural rubber can be stretched by large amounts and recovers almost completely. It is therefore often modeled by a strain energy function to correlate the stress–strain behavior under various types of deformation [1–6]. Proposed strain energy functions are often validated by comparison with early measurements by Treloar [7] of stress–strain relations in uni-axial and bi-axial stretching. Recognizing that reversibility is a prerequisite for expressing stresses and strain energy in terms only of the current deformation, Treloar paid particular attention to whether the stress at a given strain was substantially the same on unloading the specimen from a higher strain as it was when stretching the specimen. The differences were small, about 2–4% for carefully selected compounds stretched up to about 300%, but marked irreversibility was noted at higher strains. Examples of good reversibility are shown in Figs. 5.4, 5.8, and 8.16 of Ref. [8]. The onset of irreversible behavior at a strain of about 200% is shown in Fig. 10.6 of Ref. [8], and compared with the onset of irreversibility in the relation between optical birefringence and strain, leading to the conclusion that the marked irreversibility is due to strain-induced crystallization, as corroborated later by Mukherjee [9] and Toki et al. [10,11].

Treloar was careful to use materials and test conditions that maximized the reversibility of his measurements. In one case he used a special rubber compound in which rubber was crosslinked with 8% of sulfur. This caused other modifications to the polymer molecules [12,13], that delayed the onset of strain-induced crystallization. Reversible stress–strain measurements were obtained in this way for strains up to about 450% [8, p. 90]. A second, more conventional, sample consisted of latex rubber crosslinked with about 2% of sulfur. In this case, irreversible behavior started at strains of about 300%. Treloar made measurements at a higher temperature (50 °C) in order to delay the onset of strain-induced crystallization, but marked irreversibility still appeared at strains of about 400%. He therefore used only measurements at lower strains, $<300\%$, to deduce the form of the strain energy function, remarking that "the results at large strains are not reversible and do not represent equilibrium states" [8, p. 257]. Rivlin and Saunders [14], and later, Jones and Treloar [15], also used only experimental measurements in the quasi-reversible range to evaluate the strain energy function more comprehensively. It is clear that fitting measured stress–strain relations to an elastic strain energy function without demonstrating that they are substantially reversible is inadequate to validate the chosen energy function. Thus, proposed strain energy functions for natural rubber at high strains [6,16,17], and for SBR [16], silicone

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rubber and Neoprene [18], and particle-filled compounds [16,19–21], must be regarded as uncertain, because reversibility of the stress–strain measurements was not addressed. In particular, rubber compounds containing carbon black show marked stress-softening, where the stresses depend upon the prior strain history. This behavior is clearly incompatible with an elastic strain energy function, although it could be accommodated within a more general constitutive relation that includes a "damage" criterion [22,23]. We question here whether even unfilled natural rubber can be assigned a valid strain energy function at high strains, because the stress–strain behavior in simple extension is then markedly irreversible. Also, we show that rubber at high tensile strains fails to satisfy the "universal" relation between resistance to torsion and applied tensile stress derived by Rivlin [1,24], that must hold for any elastic strain energy function to be valid. This criterion was applied by Ahmadi et al. [25] to a carbon black filled rubber compound. They found that the torsional stiffness was consistently higher than the corresponding function of tensile stress over a wide range of strains, from about 10% to 250%, indicating that the stress–strain relations for this material could not be described by any elastic strain energy function.

2. Experimental

Cylindrical rubber rods of various diameters were obtained from McMaster-Carr Engineering Supply Company. They were described as being made of "soft natural rubber latex" and were found to be elastic, resilient and of low density, about 0.93 g/mL, similar to that of rubber itself. Analysis by FTIR confirmed that the material was lightly crosslinked natural rubber (93%), containing small amounts (6%) of curative residues, protective agents and processing aids and 1% of carbon black. The indentation hardness was given as 35, in agreement with the measured shear modulus, about 0.5 MPa, and consistent with a soft, lightly crosslinked, unfilled rubber compound.

The ends of the rubber rods were reinforced by wrapping them with a thin sheet of soft rubber before clamping them in the vice grips of a tensile testing machine. Stress–strain measurements in tension were then made using samples with an unstretched length of about 100 mm. The maximum extension imposed was about 500%. Although regions near the ends were subjected to a more complex stress field, they constituted only a small fraction (about 5%) of the whole sample, the bulk being stretched homogeneously.

As shown in Figs. 1 and 2, the stress–strain relations were found to be highly reversible at lower extensions, up to about 200%, but became markedly irreversible for extensions in the range 300–500%, as observed by Treloar [7,8], Mukherjee [9] and Toki et al. [10,11].

Measurements were also made of the torsional stiffness of rods at various extensions. A light horizontal bar was attached to the center of the rod and the period T was measured of small swings of the bar in the horizontal plane. The moment of inertia I of the bar about its center was chosen so that the period T of oscillation was between 1.5 and 5 s. The average value for five swings was used to calculate the torsional stiffness M per unit length of the rod in the unstrained state, from the relation:

$$M=(4\pi^2 I/T^2)(L\lambda/2) \quad (1)$$

In Eq. (1), L is one-half of the length of the rod between the clamps in the unstrained state, typically about 50 mm, and λ is the stretch ratio. Values of M are plotted against the stretch ratio in Figs. 3 and 4, for rods having diameters of 3.08 and 6.15 mm. The same variation was found in both cases. Values of M decreased as small strains were applied and then became substantially constant over the range λ=2–4, before increasing markedly as the strain was increased further, becoming about twice as large at strains approaching 500% (λ=6).

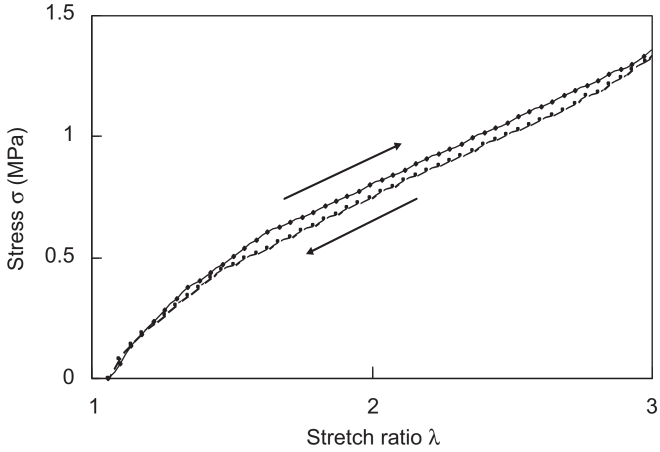

Fig. 1. Experimental stress–strain relation in tension up to 200% strain, showing reasonably good reversibility.

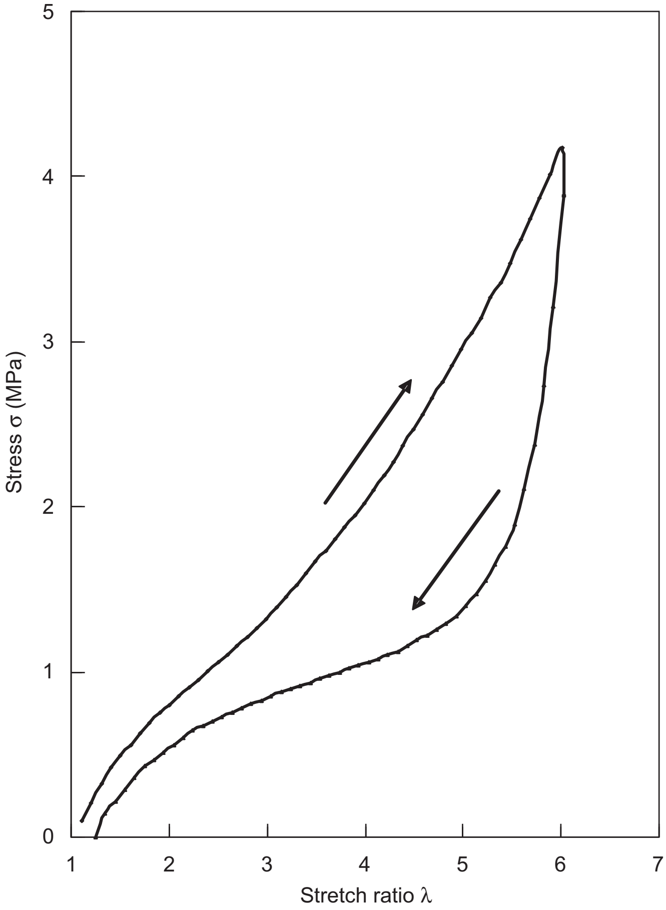

Fig. 2. Experimental stress–strain relation in tension up to about 500% strain, showing marked irreversibility.

Rivlin [1,24] derived a "universal" relation between M and a function of the tensile stress σ, denoted here S:

$$S=\sigma\pi a^4/2(\lambda-\lambda^{-2}) \quad (2)$$