

On the Form of the Strain Energy Function for a Family of SBR Materials

R. J. ARENZ, *Propulsion and Materials Research, Jet Propulsion Laboratory, Pasadena, California 91103, and Mechanical Engineering Department, Loyola Marymount University, Los Angeles, California 90045*

Synopsis

A strain energy function of the Valanis-Landel type, $W = w(\lambda_1) + w(\lambda_2) + w(\lambda_3)$, is shown to be applicable to styrene-butadiene rubber (SBR) materials having varying crosslink densities ν_e . A previously obtained functional form of the strain energy derivative $w'(\lambda)$, normalized by dividing by ν_e , is confirmed by one of the validity check plots in which a single curve represents the whole body of large-deformation test results for all degrees of biaxiality and crosslink density.

INTRODUCTION

Recent widespread interest in the strain energy function W for rubberlike materials has focused on methods of representing in a satisfactory way the complexities of the experimental dependence of the stored energy on various strain states. These complexities are illustrated by the well-known deviations at even moderate strain levels of the observed stress-strain behavior from the predictions of Gaussian statistical theory. Representations of W as a function of the strain invariants and in terms of the extension ratios are both possibilities. As examples of the first approach, there are multiple-term series expansion of James, Green, and Simpson¹ in the usual strain invariants (I_1, I_2, I_3) and a four-parameter formula of Blatz, Sharda, and Tschoegl² with the strain invariant being based on a generalized measure of strain. The second approach has been taken by Valanis and Landel³ in the form of a separable symmetric function of the principal extension ratios ($\lambda_1, \lambda_2, \lambda_3$) and by Ogden⁴ who also used a series of terms based on a generalized strain measure. (Ogden gives a good review of the methods proposed prior to his theory.) In general, isotropy and incompressibility have been assumed to apply to the elastomers under consideration in these representations.

The analytical expressions of references 1, 2, and 4 provide reasonable fits to experimental data in the examples given by the authors but require four or more constants which in several cases involve a computer approach to evaluate. Although the Valanis-Landel approach by itself does not explicitly give a mathematical expression for W , it does directly provide the complete functional form of the strain energy function. It consequently possesses the possibility of predicting the behavior of elastomers under various geometric strain states by simple

mathematical calculations and readily lends itself to comparison with experiment.

These characteristics make it appropriate to consider, in a more comprehensive way than previously, the applicability of the Valanis–Landel hypothesis to the strain energy function of styrene–butadiene rubber (SBR). Results of extensive finite deformation biaxial and uniaxial tests made at the Jet Propulsion Laboratory on a family of SBR materials have been reported previously.⁵ Stress relaxation tests of thin sheet specimens of five different crosslink densities were made in a universal biaxial tester arranged to provide varying amounts of biaxiality.⁶

In addition to the basic data, reference 5 included an indication of the functional form at equilibrium of the spatial derivative of the strain energy function, determined from strip biaxial (pure shear) data according to the Valanis–Landel approach. The necessity of verifying the general validity of the proposed strain energy function for all test geometries as well as subsequent refinement of the precise level of moduli for the SBR materials, which enters into the test of the hypothesis, motivate this further investigation. Since most of the original data furnishing the basis of this study appeared only in a foreign-published volume⁵ of the proceedings for a conference and perhaps have not received wide distribution, it may be helpful to review the pertinent experimental aspects and some of the prior data analysis forming the background of the present study.

EXPERIMENTAL ASPECTS

A full description of the apparatus and experimental procedure is available in reference 6 and details of the material composition and specimen preparation are given in reference 5. The universal biaxial relaxometer is illustrated in Figure 1, where it is shown mounted at an angle $\alpha = 16.7$ deg to the vertical axis of the Instron test machine; this is one of the six possible mounting angles available to produce various biaxial configurations. The trolleys and hooks supporting the thin-sheet test specimen along its sides are equipped with individual strain-gauged load cells to give the force distribution throughout the sheet width.

The SBR specimens had five different crosslink concentrations, given by 1, 2, 3, 4, and 5 parts by weight of the vulcanizing agent, tetramethylthiuram disulfide (TMTD), per 100 parts of Shell 1502 SBR. (These compositions are designated herein either as 1 TMTD, 2 TMTD, etc., or more simply on the figures as $n = 1, 2$, etc.) Uniaxial tensile stress–strain tests on specimens swollen to equilibrium in toluene established the elastically effective network chain density ν_e . The values of ν_e for the SBR materials are listed in Table I. The basic biaxial test specimens of SBR were molded sheets approximately 0.13 cm thick and 6.15 \times 6.15 cm square overall, with seven small reinforced holes per side to accommodate the supporting hooks.⁵

All the tests were run at room temperature (approximately 26°C), and the bulk of the data reported⁵ was for a relaxation time of 10 min. Complete mechanical characterizations were given for the SBR compositions under various biaxial strain states and to the highest strain levels attainable before failure occurred in one or more of the reinforced support holes. A typical plot showing the principal stresses σ_1, σ_2 (based on unstrained area) as functions of λ_1, λ_2 for the

TABLE I
Characteristics of SBR Vulcanizates

Specimen code ($n =$ parts TMTD)	ν_e , mole/m ³	$G(10 \text{ min})$, N/m ² $\times 10^{-5}$	G_e , N/m ² $\times 10^{-5}$
1	17.5	2.07	0.77
2	54	3.45	2.23
3	90	4.46	3.65
4	117	5.22	4.59
5	131	5.70	5.09

2 TMTD material is given in Figure 2. (Reference 5 provided plots for the 1, 3, and 5 TMTD compositions.)

Several long-time relaxation tests performed to establish the variation of stress with time indicated that the strain dependence and time dependence of stress were separable for the materials.⁵ Thus the stress relaxation data for various geometries and strain levels covering periods usually up to 10 hr (but, in a few cases, to 30 hr) could be used to obtain a reliable estimate of the equilibrium

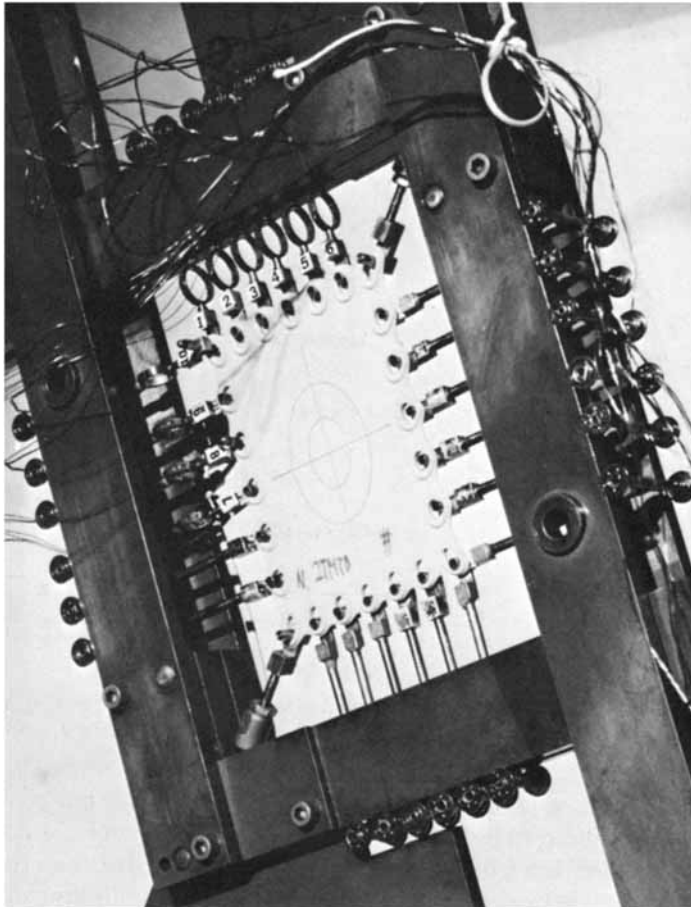


Fig. 1. Biaxial stress relaxometer, showing sample configuration, attachments with individual proof-ring load cells, and circular target used for strain measurements.

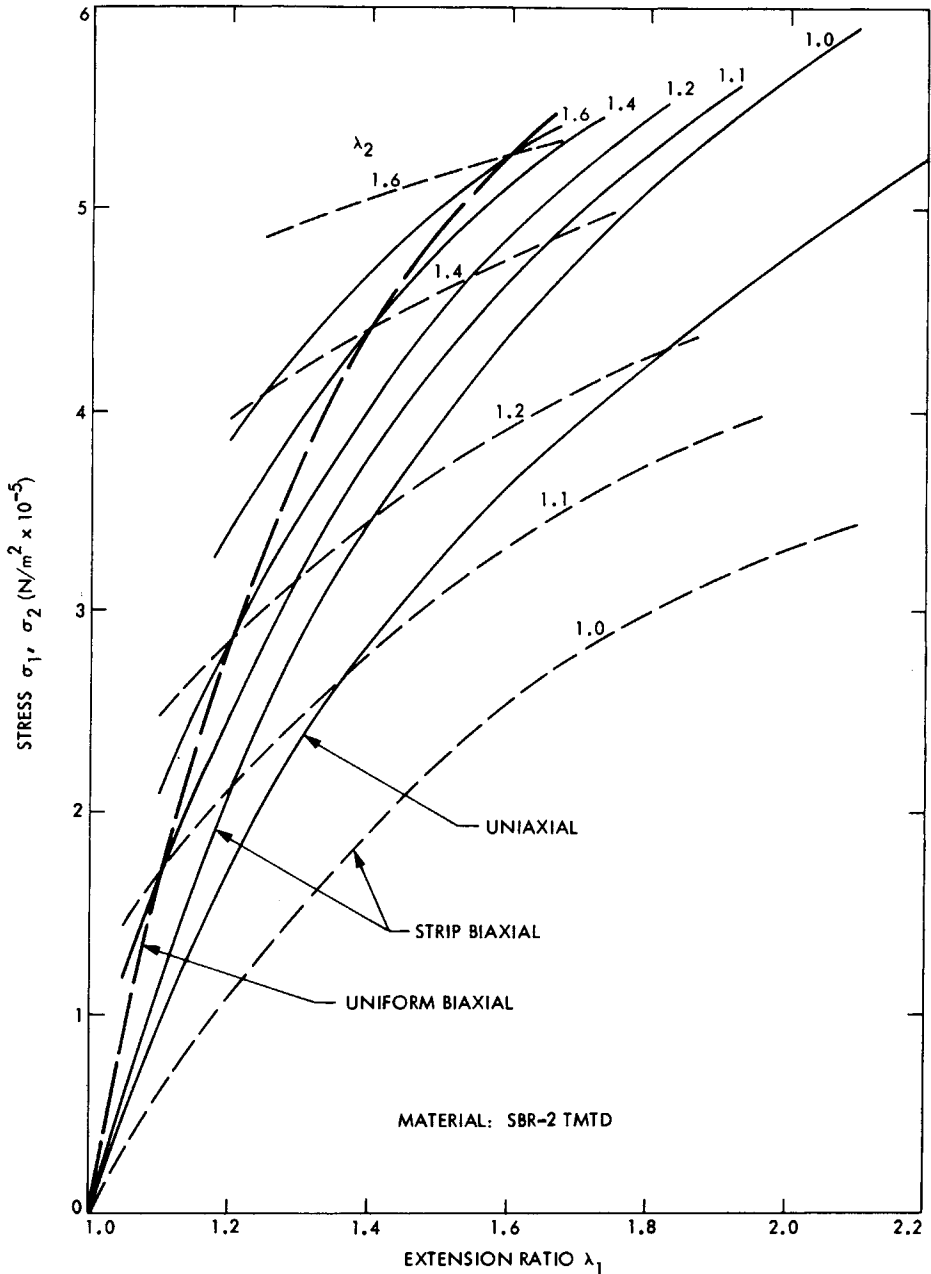


Fig. 2. Typical dependence for an SBR material of the principal stresses σ_1 (—), σ_2 (- - -) on the principal extension ratio λ_1 for various λ_2 values; relaxation time = 10 min, $T = 26^\circ\text{C}$.

behavior. For this relaxation, use was made of the power law representation which has been found to be valid for a variety of elastomers.⁷ Indeed, the accuracy of the power law extrapolation for this family of SBR materials has been verified by a reduced variable analysis⁸ involving a crosslinking density-time shifting procedure that superposes the relaxation data into a single master curve covering 16 decades of log time. The equilibrium modulus values obtained by

this wide-spectrum relaxation curve agreed within a few percent of those obtained by applying the power law to each material test history over a much shorter time span. Moreover, the equilibrium moduli for the SBR materials were in generally good agreement⁸ with those obtained for SBR with similar crosslinking levels by creep tests⁹ that established equilibrium compliance levels.

ANALYSIS BY VALANIS-LANDEL HYPOTHESIS

With estimates of equilibrium behavior, a representation of the equilibrium strain energy function could be determined for this substantially incompressible rubber by using the Valanis-Landel hypothesis³ of a separable symmetric function given by

$$W = w(\lambda_1) + w(\lambda_2) + w(\lambda_3) \quad (1)$$

where λ_1 , λ_2 , and λ_3 are the three principal extension ratios. Following the analysis given in reference 3, a functional form of $w_e'(\lambda)$, where w' denotes the derivative of w with respect to its argument and the subscript e designates the long-time equilibrium condition, was obtained for the five SBR compositions using data from strip biaxial (pure shear) tests, in which $\lambda_2 = 1$. This is the only test to explicitly determine it,^{3,5} and w' was evaluated for tensile strains ($\lambda_1 > 1$) using eq. (45) of reference 3, namely,

$$w'(\lambda_1) = \frac{t_1 - t_2}{\lambda_1} \quad (2)$$

where t_1 and t_2 are the true stresses in the principal directions in the plane of the sheet ($t_3 = 0$ for the thin-sheet specimen). It was found that the w_e' values could be normalized by dividing by the crosslinking density ν_e out to the highest strains tested. The resulting single master curve of w_e'/ν_e showed that the functional form of $W(\lambda)$ is independent of the network chain concentration. This would be expected for small strains from the Gaussian statistical theory, which predicts direct proportionality of elastic modulus to ν_e , but the inadequacy of the theory at larger deformations points to the need of approaches such as the one used here to test the applicability of scaling by ν_e .

As the emphasis in reference 5 was this correlation of strain energy function to ν_e , no thorough comparison was made there to verify that the strain energy function W derived from data corresponding to the strip biaxial (pure shear) test condition would also apply to all the biaxial strain states as well as uniaxial stress conditions. It is imperative here (as in the study of the validity of any candidate form of representation of W) to thus verify that it does, in fact, represent the behavior of the material for all loading conditions. Accordingly, it is the purpose of this paper to demonstrate that the Valanis-Landel stored energy representation is indeed a valid characterization of the family of SBR materials.

At the same time, an application of the representational method of Blatz, Sharda, and Tshoegl² to SBR¹⁰ required additional combined treatment of uniaxial tension data (also obtained in the previous experimental program⁵) and uniform biaxial tension results. The latter geometry for an incompressible material has the same state of deformation as occurs in simple compression.² It hence furnishes simple compression behavior since $t_c(\lambda_c) = -t_t(\lambda_t)$, where the

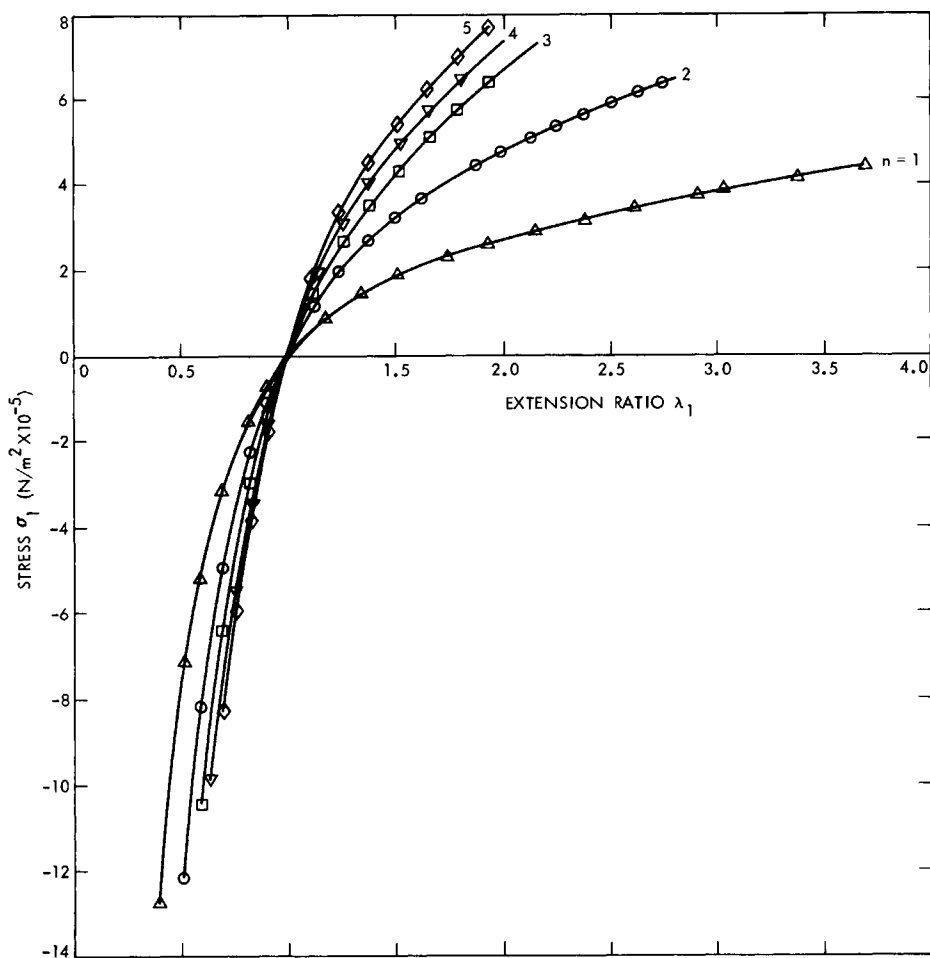


Fig. 3. Uniaxial stress-strain results at 10 min of relaxation time for SBR materials of varying crosslink density; n denotes the number of parts of TMTD crosslinking agent. Compression data derived from uniform biaxial tension tests; $T = 26^\circ\text{C}$.

subscript c refers to simple compression, the subscript t refers to uniform biaxial tension, and $\lambda_c = \lambda_t^{-2}$. The use of this "BST" strain energy function* showed the need to determine the zero strain modulus with the maximum precision possible. This is facilitated by plotting the stress-extension ratio data for both tensile and compressive strains to provide a continuous curve through the zero-strain point, as shown in Figure 3 for SBR at 10 min of relaxation time. The moduli previously reported^{5,8} for these SBR materials represented slopes of

* Since the SBR data exceeded $\lambda = 3$ in only one case (cf. Fig. 3), the material parameters in the second term of the Blatz-Sharda-Tschoegl equation² for simple extension could not be adequately established. The one-term equation, i.e., $t = (\lambda^n - \lambda^{-n/2})(2G/n)$, where t is true stress and G is the shear modulus (with the values listed in this paper) gave a value of $n = 1.32$ to very satisfactorily represent uniaxial and strip biaxial data at a relaxation time of 10 min for the five SBR compositions, indicating n to be a material parameter substantially independent of ν_e . Since $n = 2$ corresponds to statistical theory, the SBR material exhibits a λ dependence more complex than predicted by the simple theory.

stress-strain curves obtained from the tensile side only. As a result, the path through $\lambda = 1$ was not as well defined, and, in effect, the moduli approximated the average stress-strain ratio out to perhaps 5% strain. The refined values of $G(10)$, the shear relaxation modulus at 10 min, obtained by use of tangents at $\lambda = 1$ to the curves of Figure 3, are listed in Table I (where incompressibility has been used in converting Young's modulus to G). The corrected values are not significantly modified from those previously listed,⁸ but the change is discernible, being approximately 5% higher for most of the SBR compositions. (These modifications in $G(10)$ are small enough that, in conjunction with the fact that the time dependence of the relaxation process remains entirely unaltered, none of the essential conclusions previously published^{5,8} is changed. The equilibrium modulus levels given in the references should all be increased slightly, but this does not modify the results of superposition or shifting procedures of ref. 8 to a degree sufficient to require correcting.)

Analysis of the biaxial test results (e.g., as in Fig. 2) confirmed these values as applicable within a few percent experimental scatter to all the loading geometries tested for each material. For completeness, we also list in Table I the modified equilibrium shear moduli G_e corresponding to the corrected $G(10)$ values just given.

VERIFICATION OF THE STRAIN ENERGY FUNCTION

We now proceed to test the validity of the form of the strain energy function W derived from the strip biaxial test by checking the functional form in uniaxial and the rest of the biaxial test configurations. If it satisfies tests in all these geometries, then it can be truly said to characterize the material. Inasmuch as results and analysis of reference 5 proved separability of strain and time, the simpler approach will be chosen of using isochronal data at a relaxation time of 10 min since the bulk of the stress-strain data was obtained at that point in the relaxation process.

To use the isochronal approach, we first need to calculate the $w'(\lambda)$ function from strip biaxial data at 10 min of relaxation time. For positive strain ($\lambda > 1$), use is made of the λ_1 -direction data and eq. (2). For negative strains ($\lambda < 1$), use is made of strip biaxial data in the thickness, or λ_3 , direction (where $t_3 = 0$ and, since $\lambda_2 = 1$, $\lambda_3 = 1/\lambda_1$) and the applicable equation is³

$$w'(\lambda_3) = -t_2/\lambda_3 \quad (3)$$

The results for both tension and compression are shown in Figure 4, where the function $w'(\lambda)$ is now determined for the 1 TMTD material in the range of values $0.3 < \lambda < 3$, with lesser ranges for the stiffer materials.

Various empirical relations as functions of λ could be used to attempt to fit the SBR curves, such as the $2G \ln \lambda$ variation proposed by Valanis³ or the $2G[(1 - (1/\lambda))]$ form suggested by Dickie and Smith,¹¹ with varying regions of approximate representation. However, our purpose here is rather to prove the validity of eq. (1) for SBR by applying the functional forms obtained in Figure 4 to all the uniaxial and biaxial tests. To do this, we note that in accordance with the relation of stress to the strain function derivative w' resulting from eq. (1), a straight line of unit slope should be given³ by a plot of $(t_1 - t_2)/2G$ versus $(1/2G)[\lambda_1 w'(\lambda_1) - \lambda_2 w'(\lambda_2)]$, where $w'(\lambda)$ is given by the curves of Figure 4. Figure 5

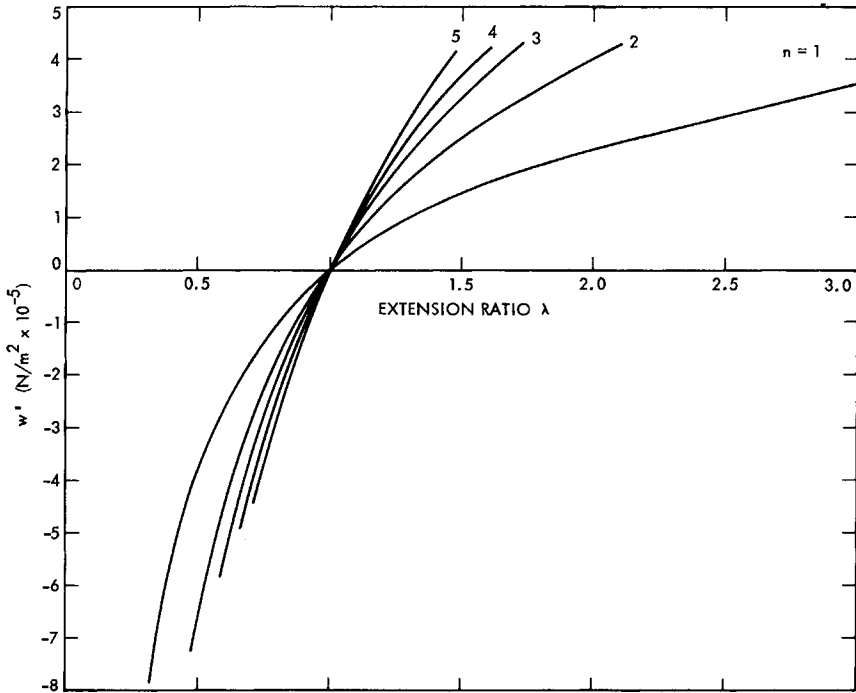


Fig. 4. Variation of $w'(\lambda)$ with λ for the materials of Figure 3 at 10 min of relaxation time; $T = 26^\circ\text{C}$.

shows this to be the case within experimental error; of all the results, only the uniaxial data at high strains appear to deviate in a systematic manner, falling a bit below the theoretically predicted line. The reason for this is uncertain, but it may stem from the difficulty in cutting uniaxial test samples from the biaxial sheet specimens; uniform widths and smooth edges are far less likely than in the case of molded specimens.

A further test of the consistency of the form of W proposed in eq. (1) follows from additional analysis of the biaxial tests. The relations between strain function and stress become³

$$(1/2G)\lambda_3 w'(\lambda_3) = (1/2G)[\lambda_2 w'(\lambda_2) - t_2]$$

and

$$(1/2G)\lambda_3 w'(\lambda_3) = (1/2G)[\lambda_1 w'(\lambda_1) - t_1]. \quad (4)$$

The right-hand sides of eq. (4) can be evaluated from test data so that the values of $\lambda_3 w'(\lambda_3)/2G$ are known and can be plotted against λ_3 , as shown in Figure 6. If the proposed form of W is valid, then the general biaxial data should lie on the curve obtained from the strip biaxial test. That this is the case within experimental error is evident from Figure 6.

Particularly powerful verification from Figure 6 lies in the fact that the abscissa λ_3 is not normalized by dividing by the relaxation modulus (as occurs on both coordinates of Fig. 5), yet the plot of data shows that essentially a single curve (obtained from strip biaxial test results) represents all the data from tests ranging

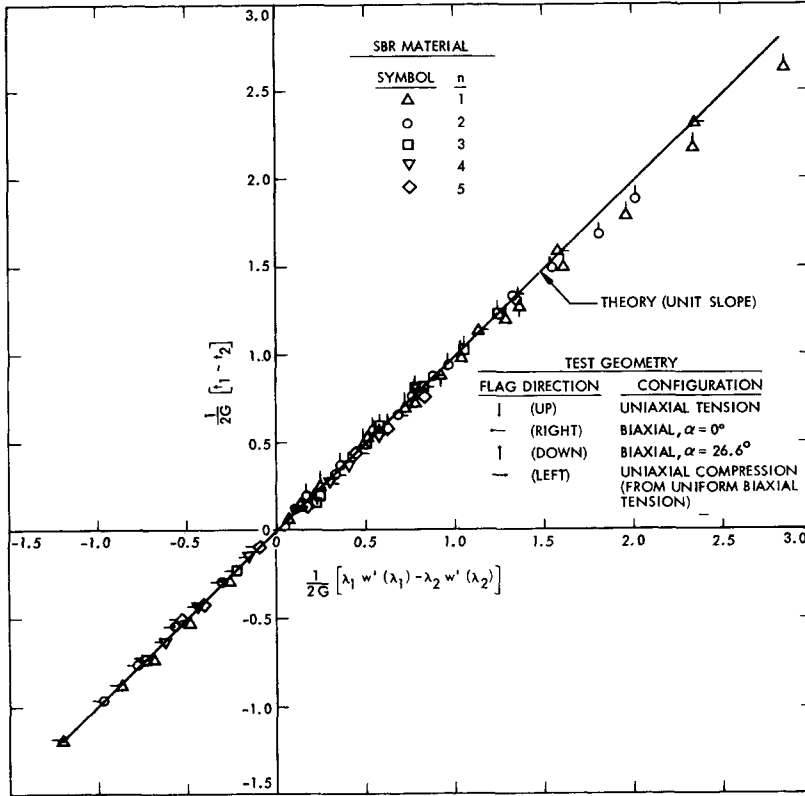


Fig. 5. Test of the basic separability hypothesis for W , showing that the stresses (or stress differences) measured in uniaxial and arbitrary biaxial conditions can be calculated from a shear modulus and the function $w'(\lambda)$ determined solely from pure shear measurements.

over various strain levels and all the possible degrees of biaxiality for all five SBR materials. Thus, the W hypothesis has been shown to be applicable not only to each individual material, but also for the whole family of materials as a system with a unified strain dependence. The latter feature confirms the previously published⁵ equilibrium w_e' master curve normalized by dividing by ν_e , which demonstrated that the functional form of $W(\lambda)$ is independent of the network chain concentration. These two factors taken together show that use of the Valanis-Landel W hypothesis is potentially capable of predicting the mechanical response of whole families of elastomeric material systems once a single member of the family has been characterized.

CONCLUSIONS

The generality of applicability and ease of use of the Valanis-Landel functional representation of W shown above indicates its value as a method of representing and determining W without a strong *a priori* constraint as to mathematical form. In some cases, however, the assumption of a specific mathematical form may offer practical advantages; in this sense, the two approaches to the determination of W may be viewed as complementary.

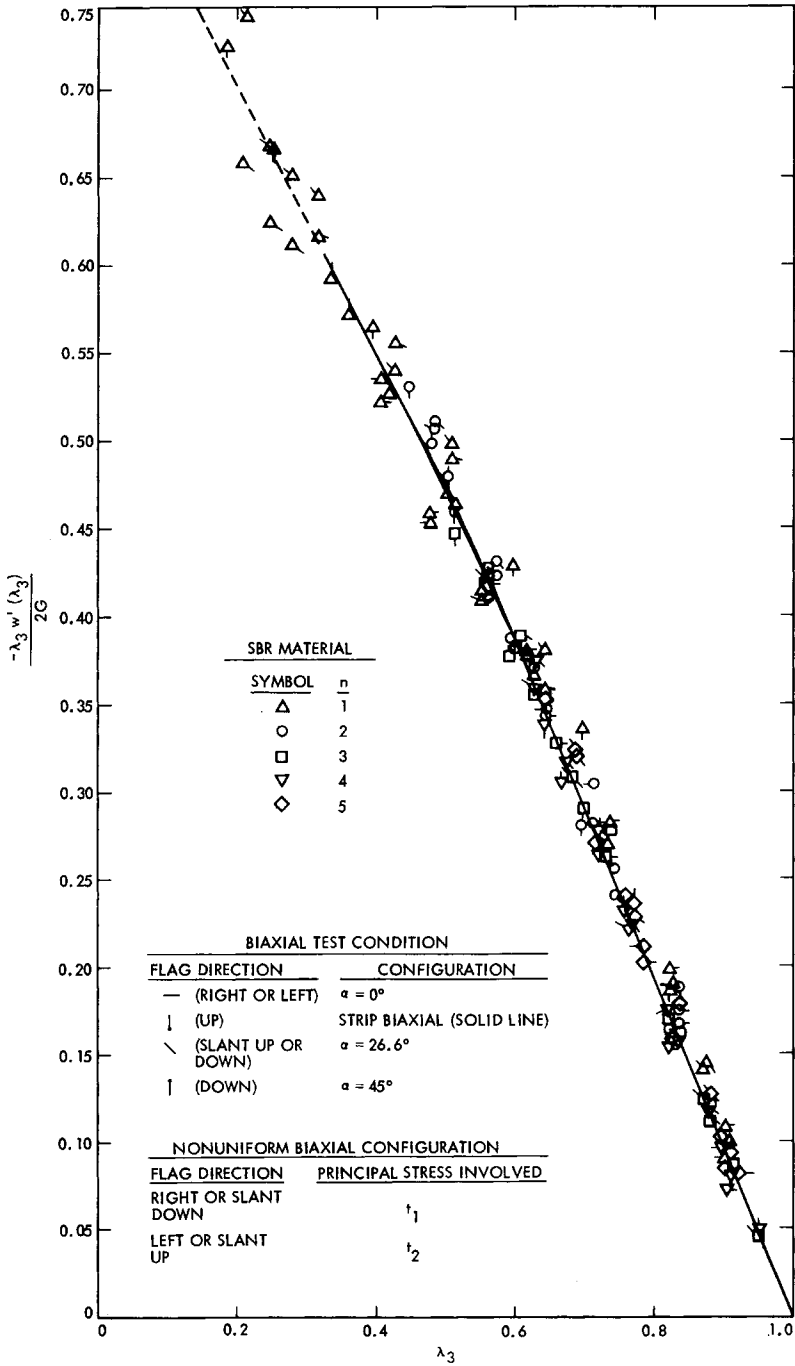


Fig. 6. Further test of the separability hypothesis for W , based on eq. (4). The strain function $\lambda_3 w'(\lambda_3)$ calculated from either λ_2 and t_2 or λ_1 and t_1 , using data from a variety of biaxial test conditions, is independent of these variations within experimental error.

It is the author's pleasure to express thanks to Dr. R. F. Landel for his encouragement and discussions during the course of this study. Gratitude is also due Dr. Kenji Tsuge, who contributed greatly in conducting the test programs which provided the data for the study. This paper represents

one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

REFERENCES

1. A. G. James, A. Green, and G. M. Simpson, *J. Appl. Polym. Sci.*, **19**, 2033 (1975).
2. P. J. Blatz, S. C. Sharda, and N. W. Tschoegl, *Trans. Soc. Rheol.*, **18**, 145 (1974).
3. K. C. Valanis and R. F. Landel, *J. Appl. Phys.*, **38**, 2997 (1967).
4. R. W. Ogden, *Proc. R. Soc.*, **A326**, 565 (1972).
5. K. Tsuge, R. J. Arenz, and R. F. Landel, in *Mechanical Behavior of Materials* (Proceedings of the International Conference), Vol. III, The Society of Materials Science (Japan), Kyoto, 1972, p. 443.
6. R. J. Arenz, R. F. Landel, and K. Tsuge, *Exp. Mech.*, **15**, 114 (1975).
7. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970, p. 439.
8. R. J. Arenz, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 131 (1974).
9. R. G. Mancke and J. D. Ferry, *Trans. Soc. Rheol.*, **12**, 335 (1968).
10. R. J. Arenz, unpublished results.
11. R. A. Dickie and T. L. Smith, *Trans. Soc. Rheol.*, **15**, 91 (1971).

Received March 13, 1976

Revised September 15, 1976