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The Internal Energy Contribution to the Restoring Force in Viscoelastic Rubberlike Materials[1]

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ABSTRACT: Incorporation of the temperature dependence of the strain parameter n in the theory of Sharda and Tschoegl predicts that the internal energy contribution to the restoring force in rubberlike materials should depend on the stretch ratio. Published data were used to support this contention. By introducing the concept of a reduced isochronal time it becomes possible to determine f_u/f on uncross-linked as well as cross-linked materials. Thus f_u/f can be followed as a function of cross-link density, temperature, and time.

I. Introduction

Elastomers can be stretched reversibly to remarkably high elongations because they consist of flexible cross-linked long chain molecules. The statistical theory of rubber elasticity[4–8] ascribes the restoring force in a deformed elastomer predominantly to the change in the configurational entropy of the chains which accompanies the deformation. Contributions from changes in internal energy are considered to play generally a subsidiary role. In natural rubber, the elastomer par excellence, internal energy changes contribute roughly one-fifth of the restoring force at elongations below about 200%. Experimentally, the magnitude of the internal energy contribution is commonly determined from measurements of the force–temperature coefficient. Such experiments are often referred to as thermoelastic studies because they assume that the elastomer under study behaves as a purely elastic body although elastomers, like all polymers, are viscoelastic. Thus, the measurements must be conducted at elastic equilibrium, i.e., in the completely relaxed state. In practice this situation can only be approached asymptomatically.

Although the relaxation processes can be accelerated by increasing the temperature, this device is limited by the possibility of thermal degradation. Therefore, thermoelastic experiments are rarely, if ever, made under conditions in which all measurements can be considered to have been obtained sufficiently close to elastic equilibrium to render negligible the error resulting from residual viscoelastic relaxation. The magnitude of the error depends not only on the experimental conditions such as temperature, waiting period, stretch ratio, etc., but also on the nature of the elastomer. Thus, the error is small for natural rubber at 0 °C but may not be so for another elastomer at the same temperature.

In a series of recent papers[9–13] we have presented a theory for the description of the viscoelastic behavior of rubberlike materials in moderately large deformations. This theory easily spans the range of deformations which are commonly employed in thermoelastic studies. It is based on the assumption that time shift invariance is preserved in moderate deformations of elastomers. In materials for which this assumption proves valid, the effects of strain and time are separable in the response to a step function of strain in simple tension, the most commonly used technique in thermoelastic measurements. In this paper we propose a method, based on this separability, which circumvents the difficulties inherent in attaining elastic near equilibrium by referring all measurements to a reduced isochronal time. We call isochronal time that time which refers the isothermal response of a polymer to the same state of relaxation. The concept of reduced isochronal time generalizes the (isothermal) isochronal time by applying to it the well known principle of time–temperature–pressure superposition. We have used isochronal time in several previous publications[11,12] in which we have denoted it by t_r. Smith[14,15] had earlier used a similar concept in reducing data obtained in ramp (constant rate of strain) experiments. We define the reduced isochronal time, t_r^*, by

$$t_r^* = t_r/a_{T,P} \tag{1}$$

where $a_{T,P}$ is the temperature and pressure function.[16,17]

In the past, thermoelastic measurements were made only on cross-linked materials because of the impossibility of attaining elastic equilibrium in uncross-linked polymers. The concept of reduced isochronal time removes this restriction. The amount of deformational energy which is stored in a viscoelastic body will depend on the particular choice of the (constant) reduced isochronal time. However, the partitioning of the stored energy into configurational (entropic) and into interchain or intrachain (energetic) parts will be such that the ratio, f_u/f, remains independent of the choice of t_r^*. Hence, it becomes possible to examine changes in the internal energy contribution as a function of temperature as well as cross-link density. The concept of reduced isochronal time also permits extension of thermoelastic studies from the rubbery into the transition region as far as the theory allows.

To illustrate the concepts introduced here we use Sharda and Tschoegl's strain energy density function for compressible materials[18,19] to represent the stress–strain relations of viscoelastic rubberlike materials at reduced isochronal time. The Sharda–Tschoegl function is an adaptation of the strain energy density function of Blatz, Sharda, and Tschoegl[20] to compressible materials. Both functions are based on the concept that each material carries its own strain measure which, if properly chosen, will greatly simplify the form of the constitutive equation.

The strain measure was assumed to be independent of temperature by Blatz, Sharda, and Tschoegl.[20] However, our recent studies indicate[11,12] that the strain measure does depend on temperature although this dependence is relatively small in natural rubber. We show in this paper that a temperature dependent strain measure implies that the relative internal energy contribution to the total restoring force is not independent of the stretch ratio even at elongations below about 200%. The prediction is in contradiction to the Gaussian statistical theory which implies that the internal energy is independent of the deformation. Careful examination of the literature data appears to support our view.

Simple tension is not the only, nor is it necessarily the most appropriate, mode of deformation for thermoelastic studies. Treloar[5] advocates the torsion–tension test. In simple tension our present theory is not applicable in the glassy region and in the upper transition region because it does not allow for volume relaxation. Such effects arising from volume dilatation in simple tension would be eliminated in shear,[17,21] but the volume relaxation incident upon cooling a specimen to lower temperatures would still persist.[21] The closer the temperature is to the glass transition temperature, the more pronounced is the effect of volume relaxation.

Thermoelastic studies are undertaken to ascertain the range of conditions over which the molecular theories of the mechanical behavior of rubberlike materials is valid. The concepts which we present in this paper are intended to broaden the range of investigation with respect to time, temperature, and pressure.

II. Thermoelastic Theory

We now proceed to develop the required basic relations. From the thermodynamics of elastic deformation, we obtain for simple tension,

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + f\mathrm{d}L \tag{2}$$

and

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V + f\mathrm{d}L \tag{3}$$

where U is internal energy, T is the temperature, S is the entropy, P is the pressure, V is the volume, f is the tensile force, L is the length of the specimen, and A is the Helmholtz free energy.

From eq 1 we can derive[7]

$$\frac{f_\mathrm{u}}{f} = \left.\frac{\partial U}{\partial L}\right|_{V,T} = 1 - \frac{T}{f}\left.\frac{\partial f}{\partial T}\right|_{V,L} \tag{4}$$

as the relative contribution to the force from the internal energy, U. Equation 4, being based solely on thermodynamics, is independent of any constitutive model.

(A) Statistical Theory. In principle, eq 4 provides a criterion for checking the validity of the statistical theory of rubber elasticity. In its current form[22] this theory gives the restoring force in simple tension as

$$f = \nu kTA_0(\langle r^2\rangle_0/\langle r^2\rangle_\mathrm{f})(\lambda - \lambda^{-2}) \tag{5}$$

where ν is the number of effective chains in the network per unit undeformed volume, k is the Boltzmann constant, A_0 is the undeformed cross-sectional area of the specimen, λ is the stretch ratio, $\langle r^2\rangle_0$ is the mean-square end-to-end distance of chains between cross-links, and $\langle r^2\rangle_\mathrm{f}$ is the same distance if the chains are freed of the constraint of the cross-links. The temperature dependence of $\langle r^2\rangle_0$ is related to the thermal expansion of the sample but $\langle r^2\rangle_\mathrm{f}$ is characteristic of the chemical structure of the chains. From eq 2 one may derive[7]

$$\frac{f_\mathrm{u}}{f} = T\frac{\mathrm{d}\ln\langle r^2\rangle_\mathrm{f}}{\mathrm{d}T} \tag{6}$$

which relates f_u to $\langle r^2\rangle_\mathrm{f}$. Equation 6 thus links thermoelastic studies to solution behavior and to the rotational isomeric state model of the behavior of chain molecules.[8,23]

From eq 4 one may derive the equation of Flory, Ciferri, and Hoeve[24]

$$\frac{f_\mathrm{u}}{f} = 1 - T\left.\frac{\partial \ln f}{\partial T}\right|_{P,L} - \frac{3\alpha_0 T}{\lambda^3 - 1} \tag{7}$$

as well as the equation of Shen and Blatz[25]

$$\frac{f_\mathrm{u}}{f} = 1 - T\frac{\mathrm{d}\ln G}{\mathrm{d}T} - \alpha_0 T \tag{8}$$

where G is the shear modulus at atmospheric pressure and α_0 is the linear thermal expansion coefficient of the undeformed material. The last two equations allow determination of f_u/f at constant pressure by invoking the statistical theory as modified by Flory.[22] It can be shown that eq 7 is equivalent to eq 8. However, due to the presence of the term $(\lambda^3 - 1)^{-1}$ in eq 7, a small experimental error in the vicinity of $\lambda = 1$, which is experimentally unavoidable, will greatly affect the calculation of f_u/f. Equation 8 has the advantage of averaging out the experimental uncertainties over the whole region of strain before calculating the value of f_u/f. Equations 6 and 8 claim that f_u/f, i.e., the relative contribution of the internal energy to the restoring force, is independent of strain. This is a direct consequence of the assumption of the Gaussian statistical theory that the relative contribution by internal energy is to be accounted for by intrachain energy alone.

To prove the validity of the modified statistical theory, measurements based only on thermodynamic considerations and completely independent of structural models and constitutive equations are needed. Equation 4 is difficult to use experimentally because determination of the force–temperature coefficient at constant volume requires imposition of large hydrostatic pressures to counteract small changes in volume. Using the appropriate Maxwell relation,[26] eq 4 can be recast as

$$\frac{f_\mathrm{u}}{f} = 1 - T\left.\frac{\partial \ln f}{\partial T}\right|_{P,L} - T\frac{\beta_{P,L}}{\kappa_{T,L}}\left.\frac{\partial \ln f}{\partial P}\right|_{T,L} \tag{9}$$

where

$$\beta_{P,L} = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_{P,L} \tag{10}$$

is the volumetric expansion coefficient at constant pressure and length, and

$$\kappa_{T,L} = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_{T,L} \tag{11}$$

is the isothermal compressibility at constant length.

By determining the force-temperature coefficient, the force-pressure coefficient, the volumetric expansion coefficient, and the isothermal compressibility at constant length, as required by eq 9, Allen et al.[27] and Sharda and Tschoegl[19] determined f_u/f for natural rubber at temperatures above 0 °C.

Allen's data give values of f_u/f which are in good agreement with values obtained from thermoelastic data carried out at constant pressure and analyzed by eq 7. This agreement, and the fact that f_u/f does not show any significant dependence either on temperature or on strain, seems to give a satisfactory confirmation of the theory. Furthermore, the reported good agreement[7] among values of d ln $\langle r^2\rangle_f$ dT obtained from thermoelastic measurements, those obtained from viscositytemperature measurements on polymer solutions, and values calculated from the rotational isomeric state theory of chain configuration provide another indication of the essential success of the theory.

(B) Phenomenological Theory. Sharda and Tschoegl[19] found good, but not complete, agreement between their data and the statistical theory. They introduced a strain energy density function[18] for compressible isotropic rubberlike materials and discussed their data in the light of a phenomenological theory based on this function. In this paper we propose a modification which takes into account the temperature dependence of the strain parameter n which, in their theory, characterizes the nonlinear stress–strain behavior.

Their strain energy density function has the form

$$W = J^{\gamma}\left\{\frac{2G}{n}\left[I_{\mathrm{E}} - \frac{3(J^{n/3}-1)}{n}\right] + \frac{K}{k}\left[(J-1) + \frac{J^{1-k}-1}{k-1}\right]\right\} \tag{12}$$

where

$$I_{\mathrm{E}} = \Sigma_{\alpha}(\lambda_{\alpha}{}^{n} - 1)/n \qquad \alpha = 1, 2, 3 \tag{13}$$

and

$$J = V/V_0 = \Pi_{\alpha}\lambda_{\alpha} \tag{14}$$

In eq 12, 13, and 14, V and V_0 are the deformed and undeformed volume, respectively, at the test temperature; V_0 is taken to be at atmospheric pressure; n is the parameter of the generalized strain measure which characterizes[20] the stress–strain relation under moderately large deformations; the parameter γ, first introduced by Tobolsky and Shen,[28,29] takes into account the dependence of the shear modulus on volume according to

$$G(J) = GJ^{\gamma} \tag{15}$$

where $G = G(1)$; K is the bulk modulus at atmospheric pressure defined by

$$K(P) = K + kP \tag{16}$$

where P is the gage pressure.

In eq 13 and 14 the stretch ratio is given by

$$\lambda_{\alpha} = L_{\alpha}(T)/L_{\alpha 0}(T) \tag{17}$$

where L_{α} and $L_{\alpha 0}$ are the deformed and undeformed length of the specimen in the principal direction α, respectively, at the test temperature, T, and $L_{\alpha 0}$ is at atmospheric pressure. The parameters n, γ, G, K, and k are independent of stress by definition and hence are independent of hydrostatic pressure also.

By the application of the principle of virtual work, we have

$$\bar{\sigma}_{\alpha} = \frac{\lambda_{\alpha}}{J}\frac{\partial W}{\partial \lambda_{\alpha}} \tag{18}$$

where $\bar{\sigma}_{\alpha}$ is the true stress in the principal direction α. For the special case of simple tension and superimposed hydrostatic pressure, we have $\bar{\sigma}_1 = \bar{\sigma} - P$, $\bar{\sigma}_2 = \bar{\sigma}_3 = P$, and $\lambda_1 = \lambda$, $\lambda_2 = \lambda_3 = \sqrt{J/\lambda}$. Substituting these into eq 12 and 18 yields

$$\bar{\sigma} = (2G/n)J^{\gamma-1}(\lambda^{n} - J^{n/2}/\lambda^{n/2}) = f\lambda/A_0J \tag{19}$$

where f is the force and A_0 is the cross-sectional area at test temperature T, at zero force, and at atmospheric pressure.

Equation 19 can be written as

$$f = A_0(T,P_0)E(T)J^{\gamma}\Psi[\lambda,n(T)] \tag{20}$$

where

$$\Psi[\lambda,n(T)] = (2/3n)(\lambda^{n} - J^{n/2}/\lambda^{n/2})/\lambda \tag{21}$$

We have assumed that $E(T) = 3G(T)$ since the bulk modulus of a soft polymer is usually about four decades higher than its shear modulus. The function Ψ depends on temperature and cross-link density through the parameter n. The effect of pressure on the restoring force appears through its effect on J and λ at constant temperature. The parameter γ may also depend on temperature and cross-link density.

We now seek an expression for $(\partial \ln f/\partial T)_{V,L}$. Taking logarithms, eq 20 can be rewritten as

$$\ln f = \ln(2/3n) + \ln E(T) + \ln A_0(T,P_0) + \gamma \ln J + \ln(\lambda^{3n/2} - J^{n/2}) - (n/2 + 1)\ln \lambda \tag{22}$$

From the definitions of G, γ, and n we have

$$\left.\frac{\partial \ln G}{\partial T}\right|_{V,L} = \frac{\mathrm{d}\ln G}{\mathrm{d}T} \qquad \left.\frac{\partial \gamma}{\partial T}\right|_{V,L} = \frac{\mathrm{d}\gamma}{\mathrm{d}T} = 0 \qquad \left.\frac{\partial n}{\partial T}\right|_{V,L} = \frac{\mathrm{d}n}{\mathrm{d}T} \tag{23}$$

where d/dT is the total differential. The assumption that $\mathrm{d}\gamma/\mathrm{d}T = 0$ is based on literature data.[8] Using eq 17

$$\left.\frac{\partial \ln \lambda}{\partial T}\right|_{V,L} = -\frac{1}{L_0(T)}\frac{\mathrm{d}L_0(T)}{\mathrm{d}T} \tag{24}$$

because of the requirement of constant $L(T)$. Equation 24 can be recast as

$$\left.\frac{\partial \ln \lambda}{\partial T}\right|_{V,L} = \frac{1}{L_0(T)}\left.\frac{\partial L_0(T)}{\partial T}\right|_{P} = -\alpha_0(T) \tag{25}$$

since L_0 is independent of pressure by our definition. The thermal expansion coefficient of the undeformed length is given by

$$\alpha_0 = \beta_0/3 \tag{26}$$

where β_0 is the expansion coefficient of the undeformed (unstressed) volume. Further

$$\left.\frac{\partial \ln A_0}{\partial T}\right|_{V,L} = -\frac{1}{A_0(T)}\left.\frac{\partial A_0(T)}{\partial T}\right|_{P} = 2\alpha_0(T) \tag{27}$$

and

$$\left.\frac{\partial \ln J}{\partial T}\right|_{V,L} = -\frac{1}{V_0(T)}\left.\frac{\partial V_0(T)}{\partial T}\right| = -3\alpha_0(T) \tag{28}$$

$$\left.\frac{\partial \ln(\lambda^{3n/2} - J^{n/2})}{\partial T}\right|_{V,L} = \frac{1}{(\lambda^{3n/2} - J^{n/2})}\left[\frac{3n}{2}\lambda^{(3n-2)/2}\left.\frac{\partial \lambda}{\partial T}\right|_{V,L} - \frac{n}{2}J^{(n-2)/2}\left.\frac{\partial J}{\partial T}\right|_{V,L}\right] + 0.5(3\lambda^{3n/2}\ln \lambda - J^{n/2}\ln J)\left.\frac{\partial n}{\partial T}\right|_{V,L} \tag{29}$$

By substituting eq 23, 25, 27, 28, and 29 into the derivative of eq 22 we obtain

$$\left.\frac{\partial \ln f}{\partial T}\right|_{V,L} = \frac{\mathrm{d}\ln G}{\mathrm{d}T} + \alpha_0(3 - 3\gamma - n) + \hat{q}(n,\lambda,J)\frac{\mathrm{d}n}{dT} \tag{30}$$

where

$$\hat{q}(n,\lambda,J) = \frac{1.5\lambda^{3n/2}\ln \lambda - 0.5J^{n/2}\ln J}{\lambda^{3n/2} - J^{n/2}} - \frac{1}{n} - \frac{\ln \lambda}{2} \tag{31}$$

At atmospheric pressure $J \simeq 1$ and, therefore,

$$\hat{q}(n,\lambda,1) = \frac{1.5\lambda^{3n/2}\ln \lambda}{\lambda^{3n/2} - 1} - \frac{1}{n} - \frac{\ln \lambda}{2} = q(n,\lambda) \tag{32}$$

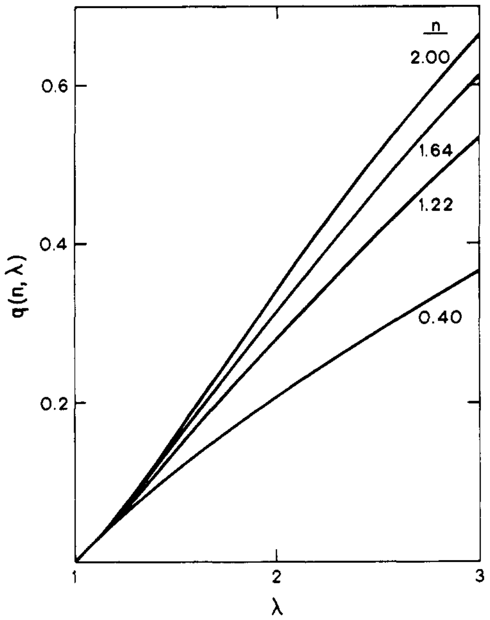

Figure 1. The function $q(n,\lambda)$ for different values of n as a function of λ.

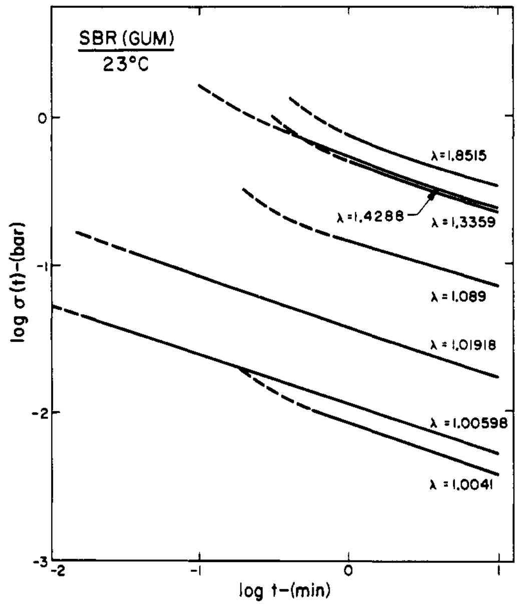

Figure 2. Engineering stress, $\sigma(t)$, as a function of time t in logarithmic coordinates. Step response of uncross-linked SBR at 23 °C.

The function $q(n,\lambda)$ is displayed in Figure 1 for $n = 2$, 1.64, 1.22, and 0.4. We notice that

$$\lim_{\lambda\to 1} q(n,\lambda) = 0 \tag{33}$$

Substituting eq 30 into eq 4 we have

$$\frac{f_\mathrm{u}}{f} = 1 - T\frac{\mathrm{d}\ln G}{\mathrm{d}T} - \alpha_0 T(3 - n - 3\gamma) - T\frac{\mathrm{d}n}{\mathrm{d}T}\hat{q}(n,\lambda,J) \tag{34}$$

We note that G must be determined strictly in accordance with the chosen definition of L_0 as discussed in the Appendix. Failure to do so can lead to appreciable error in $\mathrm{d}G/\mathrm{d}T$. The same comment applies to eq 8 also. Equation 34 agrees with the corresponding equation of Sharda and Tschoegl[19] except for the last term on the right which arises because of the temperature dependence[11,12] of n. Sharda and Tschoegl had considered this to be zero. As will be shown later, this is a good assumption for natural rubber, the material with which they were concerned.

We now turn to the determination of the parameter γ. The procedure proposed by Sharda and Tschoegl[18,19] is based on the determination of the force-pressure coefficient $(\partial f/\partial P)_{T,L}$. Because n, G, γ, L_0, A_0, V_0 are independent of pressure and so is λ at constant temperature and length, Sharda and Tschoegl derive

$$\left.\frac{\partial \ln f}{\partial P}\right|_{T,L} = \kappa_{T,L}\left[\frac{(n/2)J^{n/2}}{\lambda^{3n/2} - J^{n/2}} - \gamma\right] \tag{35}$$

Another method is suggested further on (eq 41).

One of our aims in presenting this paper is to call attention to the temperature dependence of n. This dependence leads to the prediction that f_u/f depends on the degree of deformation, as indicated by eq 34. In contrast to our prediction, most current theories, such as the Gaussian statistical theory, Shen–Blatz theory,[25] etc., conclude that f_u/f is independent of deformation. Furthermore, it is also considered to be independent of the cross-link density. There is experimental evidence, however, that f_u/f may depend both on the stretch ratio[29-37] and on the degree of cross-linking.[33] The former discrepancy may be explained partly by recognizing that measurements at low values of λ are relatively unreliable because of difficulties in measuring the initial length;[8,25] however, other literature data[31-37] seem to indicate a clear dependence on λ even when the deformations are moderately large.

The work of Sharda and Tschoegl[19] had shown that the statistical theory needs modification in two respects: it is necessary to take into account the volume (pressure) dependence of the shear modulus, and it is necessary to modify the dependence of the force on the stretch ratio. The particular modifications used by Sharda and Tschoegl are not unique but simple and appear to be adequate.

III. Viscoelastic Theory

We now extend our themoelastic treatment to viscoelastic materials. To this end we make use of the concept of the separability of strain and time effects in the response to a step function of strain.[9-12] At the test temperature and pressure the restoring force in a material of cross-link density ν (which may be zero) can be written

$$f(t_\mathrm{r},\lambda_\mathrm{r},T,P;\nu) = A_0(T,P_0)\hat{E}(t_\mathrm{r},T,P;\nu)\psi(\lambda_\mathrm{r},T) \tag{36}$$

where $\hat{E}$ is the uniaxial relaxation modulus, ψ is a suitably formulated strain function which vanishes as $\lambda \to 1$, and $A_0(T,P_0)$ is the area measured at atmospheric pressure and at the test temperature T as required by our definition of the reference state in eq 17.

A step function of strain requires an infinitely fast pulling rate during the imposition of the strain. In practice, it is approximated by a fast but finite pulling rate. Therefore, the true response to a step function of strain is achieved only after the initial ramp transients have died out. According to eq 36, curves of the responses to different strains as functions of time in logarithmic coordinates are parallel to each other. A typical example is shown in Figure 2 which displays data on an uncross-linked SBR at 23 °C and at atmospheric pressure.[9] The engineering stress, σ, in Figure 2 is defined as f/A_0.

From Figure 2 we may take an isochronal cut at t_r and crossplot the engineering stress vs. λ_r as illustrated in Figure 3. From this crossplot we can separate the uniaxial relaxation modulus $\hat{E}(t_\mathrm{r},T,P;\nu)$ from $\psi(\lambda_\mathrm{r},T)$. For the class of materials

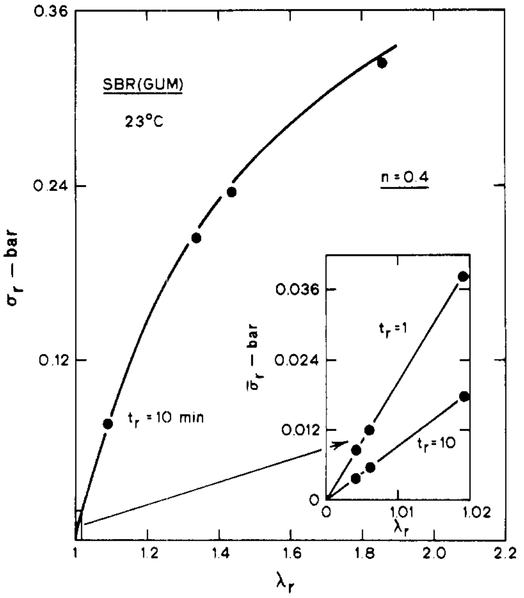

Figure 3. Stress as a function of stretch ratio at the isochronal time t_r = 10 min. Uncross-linked SBR at 23 °C.

we are now considering we may use the Sharda–Tschoegl potential function. Thus

$$\psi(\lambda_r,T) = \Psi[\lambda_r,n(T)] \tag{37}$$

When the experiments are conducted at atmospheric pressure, $J \simeq 1$. The parameter n and $\hat{E}(t_r,T,P;\nu)$ can then be determined by nonlinear least-squares fitting of data such as those displayed in Figure 3.

One may then conduct similar experiments at different temperatures, keeping the pressure constant. Therefore, n can be determined as a function of temperature. Simultaneously, one obtains segments of $\hat{E}(t_r,T;P_0,\nu)$ at various temperatures. In the next step one determines the relaxation modulus master curve at the reference temperature T_0 and the pressure P_0. The horizontal shift factor a_T and the vertical shift factor $p(T;T_0)$ can be obtained from the $\hat{E}(t_r,T;P_0,\nu)$ segments by the standard procedure used for thermorheological simple materials.[17,38] We call $E(t_r{}^*;T_0,P_0,\nu)$ the master curve. It is defined by

$$\hat{E}(t_r,T;P_0,\nu) = p(T;T_0)E(t_r{}^*,a_T;T_0,P_0,\nu) \tag{38}$$

We then perform similar experiments at constant temperature but at various pressures and determine the horizontal shift factor a_P and the vertical shift factor $\bar{p}(P;P_0)$. For piezorheologically[17] simple materials one must obtain the same master curve as that defined by eq 38. Thus we have

$$\hat{E}(t_r,P;T_0,\nu) = \bar{p}(P;P_0)E(t_r{}^*,a_P;T_0,P_0,\nu) \tag{39}$$

Considering that both the constant temperature and the constant pressure experiments should yield the same master curve and invoking[17] the free volume theory allows us to combine eq 38 and 39 to give

$$\hat{E}(t_r,T,P;\nu) = p(T;T_0)\bar{p}(P;P_0)E(t_r{}^*,a_{T,P};T_0,P_0,\nu) \tag{40}$$

Obviously, this procedure of determining $a_{T,P}$, p, and $\bar{p}$ is to some extent arbitrary because of uncertainties in the experimental data. The precision of the procedure can be improved by conducting both constant temperature and constant pressure experiments.[17]

It follows from eq 15 that

$$\bar{p}(P;P_0) = G(J)/G(1) = J^{\gamma} \tag{41}$$

But $J \simeq 1 + 3\Delta L/L_0$. Hence, J can be obtained by monitoring the length for which the force is zero at various pressures, and γ can be obtained from experimental determinations of $\bar{p}(P;P_0)$. Equation 41 is valid in shear. However, in the rubbery state, $G = E/3$ with excellent approximation. The volume ratio determined by the above procedure is not at constant reduced time $t_r{}^*$. However, the rate of volume relaxation is very fast in the materials we are interested in. Thus the error may be deemed negligible. By combining eq 36, 40, and 41 we obtain

$$f(t_r,\lambda_r,T,P;\nu) = A_0(T,P_0)E(t_r{}^*,a_{T,P};T_0,P_0,\nu) \times p(T;T_0)J^{\gamma}\Psi(\lambda_r,T) \tag{42}$$

According to eq 42 the dependence of the force on t_r for given T and P becomes a dependence on $t_r{}^*$ referred to T_0 and P_0. Hence, eq 42 expresses the fact that f_u/f is independent of time at the reduced isochronal time $t_r{}^*$. Equation 4 can thus be restated as

$$\left.\frac{f_u}{f}\right|_{t_r{}^*} = 1 - T\left.\frac{\partial \ln f}{\partial T}\right|_{V,L,t_r{}^*} \tag{43}$$

The changes in force with temperature must be measured at constant volume and length and at the same reduced time. As mentioned earlier, the constant volume condition is extremely difficult to meet. Hence, we have to use an equation similar to eq 9 to determine the relative internal energy contribution to the restoring force at constant reduced time experimentally. The equation has the form

$$\left.\frac{f_u}{f}\right|_{t_r{}^*} = 1 - T\left.\frac{\partial \ln f}{\partial T}\right|_{P,L,t_r{}^*} - T\frac{\beta_{P,L,t_r{}^*}}{\kappa_{T,L,t_r{}^*}}\left.\frac{\partial \ln f}{\partial P}\right|_{T,L,t_r{}^*} \tag{44}$$

where now the volumetric expansion coefficient and the isothermal compressibility are also measured at the reduced isochronal time $t_r{}^*$. To use eq 44 we thus require experimental values of $(\partial \ln f/\partial T)_{P,L,t_r{}^*}$, $(\partial \ln f/\partial P)_{T,L,t_r{}^*}$, and $\beta_{P,L,t_r{}^*}$ and $\kappa_{T,L,t_r{}^*}$.

The determination of $\partial \ln f/\partial T$ and $\partial \ln f/\partial P$ is similar to that of the vertical shifts $p(T;T_0)$ and $\bar{p}(P;P_0)$. The only difference is that for these partial derivatives we do not compare moduli but forces at constant length L. We can measure β and κ by monitoring the lateral dimensions, or the volume, in the experiments in which $\partial \ln f/\partial T$ and $\partial \ln f/\partial P$ are determined. Simultaneously, we also obtain the information necessary for the determination[18] of γ by the use of the reduced time form of eq 35. This can be used to check the accuracy of the determination of γ by eq 41.

Substituting eq 37 and 42 into eq 43, we obtain

$$\left.\frac{f_u}{f}\right|_{t_r{}^*} = 1 - \frac{\mathrm{d}\ln p(T;T_0)}{\mathrm{d}\ln T} - \alpha_0 T(3 - n - 3\gamma) - q(n,\lambda)\frac{\mathrm{d}n}{\mathrm{d}T} \tag{45}$$

where α_0 is the thermal expansion coefficient at constant reduced isochronal time $t_r{}^*$. In theory this can be determined from

$$\alpha_0 = \lim_{L \to L_0} \beta_{P_0,L,t_r{}^*} \tag{46}$$

We note that in the soft rubbery region $\beta_{P,L,t_r{}^*}$ and $\kappa_{T,L,t_r{}^*}$ will be nearly independent of $t_r{}^*$. This considerably simplifies their determination.

The values of $(f/f_u)_{t_r{}^*}$ predicted by eq 45 can be checked by comparison with the experimental values obtained from eq 44.

In thermoelastic measurements assuming near elastic equilibrium the force-temperature coefficient can be determined along any of several paths. The customary path is to change the temperature at several fixed lengths and to measure the resulting (equilibrium) force. If near elastic equilibrium is not attained, the requirement that one must work at constant reduced isochronal time, t_r^*, limits the choice of paths. The path usually followed in thermoelastic measurements is not convenient because of difficulties in defining the temperature history of the specimen and, hence, t_r^*. The procedure outlined in this section automatically leads to data at constant t_r^*.

Finally, we must consider the effect of cross-link density on the internal energy contribution. The statistical theory of rubber elasticity gives

$$G = \nu kT\langle r^2\rangle_0/\langle r^2\rangle_f = E_e/3 \tag{47}$$

where ν is deemed to be independent of temperature at constant volume. Both $\langle r^2\rangle_0$ and $\langle r^2\rangle_f$, however, are temperature dependent. For convenience, eq 47 can be generalized to

$$E_e = 3\zeta k\theta(T;\zeta) \tag{48}$$

where ζ is a temperature independent parameter, and $\theta(T;\zeta)$ is an unspecified function of temperature. Equation 48 would also account, e.g., for a possible temperature dependence of entanglements.[16] Substituting this into eq 45 we obtain

$$\left.\frac{f_u}{f}\right|_{t_r^*,\zeta} = 1 - \frac{d\ ln\ \theta(T;\zeta)}{d\ ln\ T} - \alpha_0 T(3 - n - 3\gamma) - q(n,\lambda)T\left.\frac{\partial n}{\partial T}\right|_{\zeta} \tag{49}$$

Equation 49 implies that the effect of changes in cross-link density will only manifest itself through changes in $\mathrm{d}\theta(T;\zeta)/\mathrm{d}T$ and through possible changes in α_0, γ, n, and $\partial n/\partial T$.

IV. Discussion

We now proceed to consider published data on f_u/f in light of the theory developed in the preceeding sections.

(A) Natural Rubber (NR). We begin with a discussion of NR data. It is known (see, e.g., ref 39) that the stress–strain relations predicted by the statistical theory are not well obeyed by NR. It is claimed,[7] however, that the behavior of this material closely conforms to the predictions of the statistical theory with respect to f_u/f. This claim is based primarily on the alleged independence, demanded by the theory, of f_u/f on the stretch ratio, swelling ratio, and cross-link density. We discuss these in turn.

Stretch Ratio. Our discussion is confined to values of λ below about 3. We consider primarily the data of Allen et al.[27] and those of Sharda and Tschoegl.[19] These represent the only attempts so far on any elastomer to determine f_u/f by using eq 3. From the experimental procedures followed it is clear that these data were obtained at near elastic equilibrium.

Allen and co-workers presented data for NR samples of various cross-link densities. The data obtained with their sample A with M_c = 26 400 can be fitted best by eq 34 in the form

$$f_u/f = 0.178 - 0.33q(1.15,\lambda) \tag{50}$$

We estimated the parameter n from the Mooney–Rivlin constants C_1 and C_2 supplied by Allen et al. using the nomograph presented elsewhere.[12] From eq 50 and 34 we obtain $\mathrm{d}n/\mathrm{d}T \simeq 0.001/°\mathrm{C}$. The plot is shown in Figure 4. For their sample D with M_c = 13 300, the best fit is obtained by assuming $\mathrm{d}n/\mathrm{d}T = 0$. For some of their other samples $\mathrm{d}n/\mathrm{d}T$ is negative.

Sharda and Tschoegl applied eq 34 to their data on natural rubber using $n = 1.64$ and assumed $\mathrm{d}n/\mathrm{d}T = 0$. The fit of their data can be improved, however, using eq 34 in the form

$$f_u/f = 0.26 - 0.116q(1.64,\lambda) \tag{51}$$

from which $\mathrm{d}n/\mathrm{d}T \simeq 0.0004/°\mathrm{C}$. This value is so small that it could not be obtained from near-equilibrium measurements in simple tension. Plots of f_u/f vs. λ for the sample used by Sharda and Tschoegl are also shown in Figure 4. We infer that for natural rubber $\mathrm{d}n/\mathrm{d}T$ is small and, consequently, f_u/f is sensibly independent of the stretch ratio, even though the sensitive scale on which the data are plotted in Figure 4 would seem to indicate otherwise.

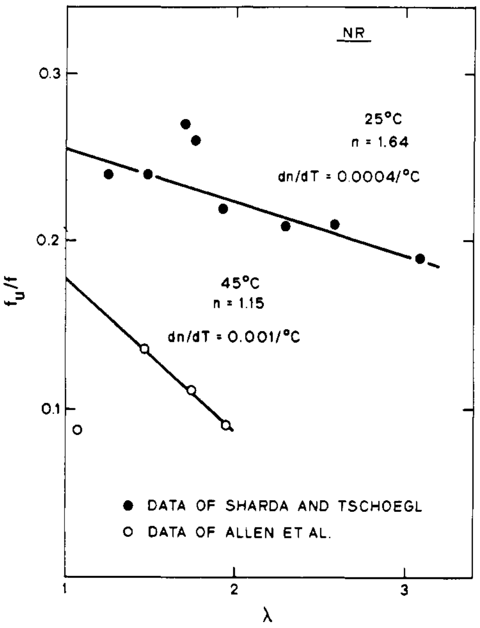

Figure 4. f_u/f as a function of λ for natural rubber at 25 and 45 °C, respectively. Data of Sharda and Tschoegl[19] and of Allen et al.[27]

Boyce and Treloar[40] determined M_u/M, where M_u is the internal energy contribution to the restoring torsional couple M, by Treloar's[41] ingenious torsion–tension test. Data obtained in this test are independent of any constitutive assumption as are data based on eq 3. Their data on NR show a definite dependence on the angle of torsion, ϕ, equivalent to a dependence of f_u/f on λ. Boyce and Treloar[40] averaged over this dependence, considering it to be within the experimental error.

Roe and Krigbaum[42] and Tanaka et al.[43] estimated f_u/f from eq 7. This equation tests the statistical theory only inasmuch as the term $3\alpha_0 T/(\lambda^3 - 1)$ is derived from eq 5. Nevertheless, their data show a slight but definite dependence of f_u/f on λ. Roe and Krigbaum[42] attempted to explain this through the dependence of the Mooney–Rivlin constants C_1 and C_2 on temperature. This is analogous to our attempt to explain the same observation through the temperature dependence of n. As pointed out elsewhere, the so-called Mooney–Rivlin equation is not a constitutive equation.[12,44]

Swelling Ratio. The Gaussian statistical theory assumes that changes in the internal energy at constant volume arise solely from intramolecular interactions. This assumption may be tested by changing the intermolecular interactions in the network by swelling with inert solvents and observing whether f_u/f changes. In studies on NR swollen in n-decane[27] and in n-hexadecane[29] it was found that f_u/f was essentially independent of the degree of swelling, q, and of the solvent used.

According to our theory the degree of swelling should have an influence on f_u/f through the parameters $\mathrm{d}\ln G/\mathrm{d}\ln T$, n, $\mathrm{d}n/\mathrm{d}T$, and γ in eq 34. Shen[29] has shown that f_u/f changes very little with the degree of swelling from q = 1.0 to 1.5. Inferring[11,39] n again from the values of C_2/C_1, we deduce that n increases with q. Nothing is known at present about the effect of q on γ. We suspect that compensatory effects weaken the dependence of f_u/f on q. This is in accord with the findings

Table I
Values of Relative Internal Energy Contribution (f_u/f) to the Restoring Force in Natural Rubber

f_u/f	G, bar	T, °C	λ	X link	Exptl	Ref
0.107	1.69[a]	30	1.08 → 1.948	DCP	A	27
0.145	2.69[a]	30	1.474 → 1.982	DCP	A	27
0.143	4.50[a]	30	1.180 → 1.902	DCP	A	27
0.120	2.64[a]	30	1.445 → 2.095	DCP	A	27
0.123	4.57[a]	30	1.130 → 1.484	DCP	A	27
0.23	5.87	25	>1.25	S	A	19
0.126	3.7	20	1.13 → 1.25	DCP	B	40
0.18		50	1.42 → 2.58	Rad	C	46
0.13	2.09	30	1.0 → 2.0	DCP	C[b]	25
0.33	2.10	30	1.0 → 2.0	DCP	C[c]	25
0.18	5.97	30	1.0 → 2.0	DCP	D	29
0.15	5.97	30	1.0 → 2.0	DCP	C	29
0.88	4.62	30	0.9 → 1.7	DCP	D	47
0.18	3.9[a]	30	>1.30	Rad	C	48
0.18	4.1[a]	30	>1.30	Rad	C	48
0.18	3.1[a]	30	>1.30	DCP	C	48
0.18	5.2[a]	30	>1.30	S	C	48
0.35		44	2.0–3.6	DCP	E	56
0.25	3.49[a]	45	1.3	Rad	C	42
0.11	3.49[a]	45	2.5	Rad	C	42
0.215		50	1.0275	S	C	43
0.068		50	2.76	S	C	43

[a] Obtained from the Mooney–Rivlin constants C_1 and C_2. [b] Butt jointed sample. [c] Sandwiched sample.

of Allen et al.[27] that the effect of the swelling ratio on f_u/f is not a sensitive test of the statistical theory.

Cross-Link Density. Equation 6 implies that f_u/f should be independent of cross-link density provided that the length of chains between cross-links is large enough. By contrast, our theory again predicts a dependence of f_u/f on the cross-link density through d ln $\theta(T;\zeta)$/d ln T, n, $\partial n/\partial T$, α_0, and γ.

The effect of increasing concentrations of dicumyl peroxide on the internal energy contribution in natural rubber was studied by Shen et al.,[45] Allen et al.,[27] and Göritz and Müller.[56] Their data do not show any discernible change in f_u/f over most of the region they covered.

In Table I we assembled literature data on f_u/f for natural rubber. The second column contains the value of the equilibrium shear modulus which may be taken as a measure of cross-link densities. The fourth column contains the range of stretch ratios over which the f_u/f values were averaged to produce the entry in the first column. Columns 3, 5, and 7 are self-explanatory. In column six we listed the experimental method used to obtain f_u/f. The meaning of the symbols is as follows: (A) simple tension at constant V and L; (B) torsion-tension at constant P, L, and ϕ; (C) simple tension at constant P and L; (D) simple tension at constant P and T; (E) calorimetry. The data assembled in Table I show considerable scatter. This is probably explained in part by the use of different samples, experimental methods, and conditions (e.g., temperatures, stretch ratios, etc.) and different equations for calculating f_u/f. They do not indicate a definite trend in f_u/f with cross-link density for natural rubber. However, the range of moduli and, hence, degree of cross-linking which were covered in these studies is not extensive (1–6 bar). At lower or higher values of the modulus the situation may be different. Thus, Shen et al.[45] mentioned that their sample with the lowest cross-link density (0.5 phr dicumyl peroxide) exhibited an increase in the f_u/f value over that of the other samples. At higher cross-link densities than those covered in Table I we have no information on n, $\partial n/\partial T$, α_0, or γ. However, we do have values of d ln G/d ln T, the dominant term in eq 34, as a function of G from the work of Wood.[49] These data are displayed in Figure 5. We infer from these data and eq 34 that f_u/f should decrease with increasing cross-link density for moduli higher than about 7 bar. It has been shown by Katz and Tobolsky[50] that very highly cross-linked polymer networks show no glass transition; i.e., they are essentially polymeric glasses. It is known that d ln G/d ln T is negative for glasses. Hence we suspect that d ln G/d ln T would have become negative if Wood had used even higher concentrations of dicumyl peroxide. Thus, we conjecture that f_u/f might show a minimum as a function of cross-link density.

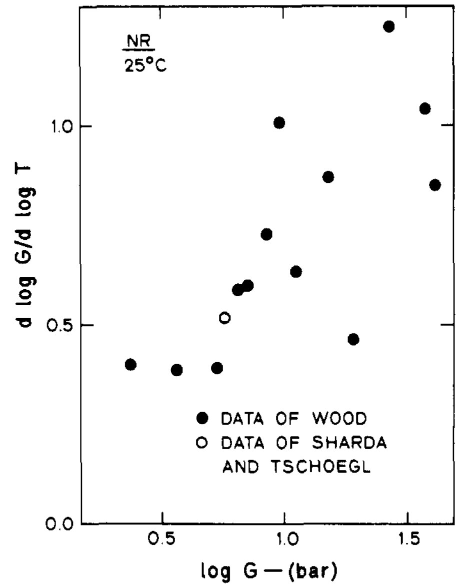

Figure 5. d ln G/d ln T as a function of log G for natural rubber at 25 °C. Data of Wood.[49]

Wood[51] found that dG/dT was constant with temperature and considered this a vindication of the Gaussian statistical theory. We point out that the Gaussian statistical theory does not require a constant dG/dT and a constant dG/dT does not imply Gaussian behavior. Differentiation of eq 47 gives

$$\frac{1}{G}\frac{dG}{dT} = \frac{1}{\nu}\frac{d\nu}{dT} + \frac{1}{T} + \frac{d\ln\langle r^2\rangle_0}{dT} - \frac{d\ln\langle r^2\rangle_f}{dT} \qquad (52)$$

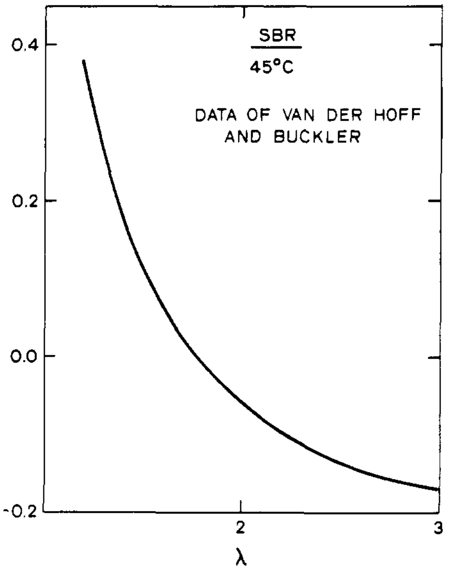

Figure 6. f_u/f as a function of λ for SBR at 45 °C. Data of Van der Hoff and Buckler.[31]

But d ln ν/dT = −d ln V_0/dT by the definition of ν, and $\langle r^2\rangle_0$ is proportional to the undeformed cross-sectional area at the test temperature. Hence d ln $\langle r^2\rangle_0$/dT = $2\alpha_0$ and

$$\frac{dG}{dT} = G\left[\frac{1}{T} - \alpha_0 - \frac{d\ln\langle r^2\rangle_f}{dT}\right] \tag{53}$$

Thus dG/dT will not in general be independent of temperature, and its constancy cannot be considered a vindication of the Gaussian statistical theory.

(B) Other Elastomers. Van der Hoff and Buckler[31] showed that f_u/f depends on the stretch ratio for a series of materials. These include *cis*-1,4-polybutadiene, poly(dimethylsiloxane), isoprene–acrylonitrile rubber, ethylene–propylene rubber, and polyisobutylene. Here we shall discuss primarily the effect of stretch ratio on f_u/f for some other elastomers. Few data are available on the effect of the degree of cross-linking.

Styrene–Butadiene Rubber (SBR). Van der Hoff and Buckler[31] calculated f_u/f for a cross-linked SBR from older data of Stearns and Johnson.[52] The plot of f_u/f vs. λ is shown in Figure 6 and indicates a strong dependence of the relative internal energy contribution to the restoring force in this material on the stretch ratio.

In another paper[11] we have presented data on the dependence of the equilibrium tensile modulus, E_e, and of n on the temperature for a cross-linked SBR. Figure 7 shows plots of f_u/f vs. λ predicted from eq 34 for this material at three temperatures. The values of n shown in Figure 7 were taken from our earlier paper. We used $\alpha_0 = 2.8 \times 10^{-4}$/°C as determined for their SBR sample by Cirlin et al.[53] Since we do not know the value of γ for this material, we assume that $\gamma = 0$. The curve at 23 °C lies between those at −10 and −40 °C. We have no explanation for this inversion at this time.

We have also studied an uncross-linked (gum) SBR for which $n \simeq 0.6$. The temperature dependence of n and of G for this material is quite weak over the range studied, i.e., from −40 to 23 °C. Thus f_u/f is virtually independent of λ. Using $\gamma = 0$ and $\alpha_0 = 2.8 \times 10^{-4}$/°C, we obtained the unexpectedly high value of $f_u/f = 0.79$ at 30 °C.

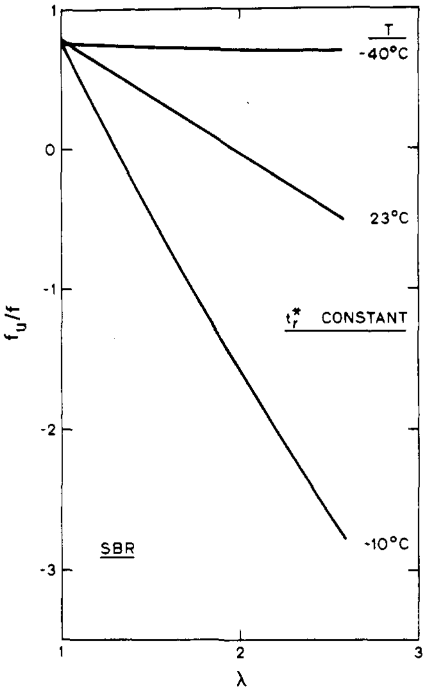

Figure 7. Predicted values of f_u/f as a function of λ for SBR at constant isochronal reduced time, at −40, −10, and 23 °C.

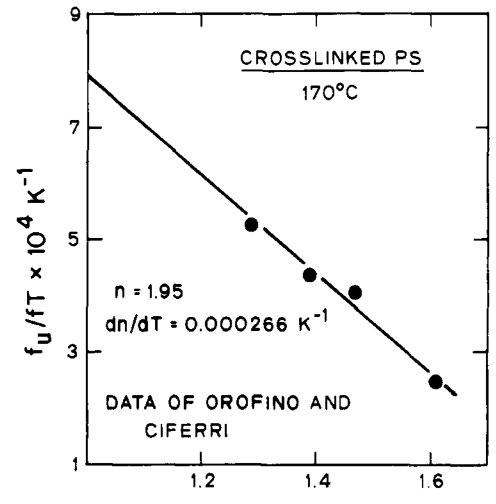

Figure 8. f_u/fT as a function of λ for cross-linked polystyrene at 170 °C. Data of Orofino and Ciferri.[36]

Viton A. Roe and Krigbaum[32] published f_u/f data on Viton A calculated from eq 7 instead of the strictly thermodynamic eq 3 or 9. Viton A is a copolymer of vinylidene fluoride and hexafluoropropylene. Equation 7, being based on the statistical theory, assumes $n = 2$ but Roe and Krigbaum's force-elongation data at T = 45 °C are better represented by assuming $n = 1.48$. The best fit of their data in terms of our theory results as

$$f_u/f = -0.1 - 1.143q(1.48,\lambda) \tag{54}$$

which gives dn/dT ≃ 0.0036 °C. We could have recalculated the data according to the appropriate equations.[19] However, this would not have affected the conclusion that here, as in SBR, f_u/f depends on the stretch ratio.

Cross-Linked Polystyrene. Orofino and Ciferri[36] presented data on polystyrene cross-linked with divinylbenzene. The best fit of their force-elongation data gives $n = 1.95$. The data are best represented by

$$f_u/fT = 7.85 \times 10^{-4} - 0.002\,66q(1.95,\lambda) \tag{55}$$

Thus dn/dT = 0.002 66/°C. Both the data and the fit are shown in Figure 8 in which f_u/fT is plotted on the ordinate instead of f_u/f. The data again show a dependence on λ.

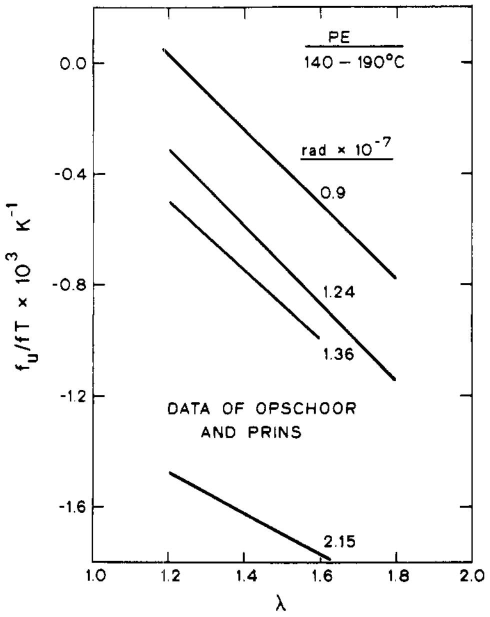

Figure 9. f_u/fT as a function of λ for cross-linked polyethylene at 140–190 °C. Data of Opschoor and Prins.[33]

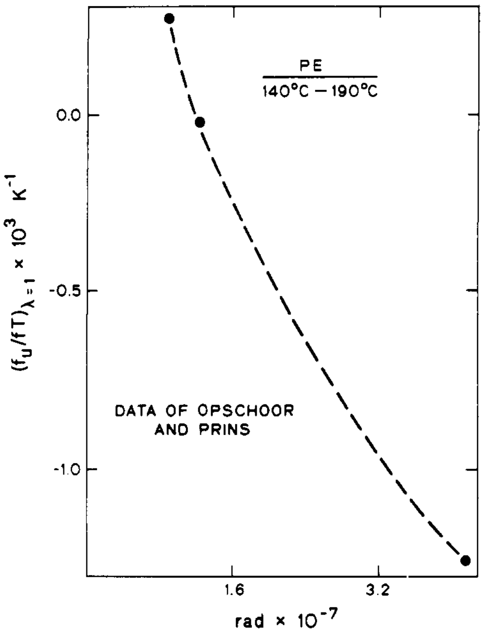

Figure 10. f_u/fT as a function of the radiation dose for cross-linked polyethylene at 140–190 °C. Data of Opschoor and Prins.[33]

Cross-Linked Polyethylene. Opschoor and Prins' data[33] on radiation cross-linked polyethylene show a clear dependence of f_u/f on the stretch ratio as shown in Figure 9 in which again f_u/fT is plotted as a function of λ for samples with different cross-link densities. Their force-elongation data indicate that $n \simeq 2.0$ for cross-linked polyethylene. The values of dn/dT range from 0.0025 to 0.0041.

A plot of $(f_u/f)|_{\lambda=1}$ against the γ radiation dose is shown in Figure 10. The curve shows a strong dependence of $(f_u/f)|_{\lambda=1}$ on cross-link density. At $\lambda = 1$, $q(n,\lambda)$ is equal to zero and, hence, according to eq 49, the change in f_u/f due to the difference in cross-link density should arise from changes in $d \ln \theta(T;\zeta)/dT$, α_0, n, and γ. It appears that in polyethylene $d \ln \theta(;\zeta)/dT$ depends on the cross-link density. This is consistent with Wood's data on natural rubber (see Figure 5).

(C) Conclusions. In NR f_u/f data appear to agree with the predictions of the Gaussian statistical theory of rubber elasticity. However, one must bear in mind that swelling measurements do not afford a sensitive test, that there is a small but probably real dependence on the stretch ratio, and that there are indications that f_u/f may depend on the cross-link density outside of the range that has so far been investigated.

The picture is different if we consider other elastomers. A definite dependence on the stretch ratio appears to be discernible in a number of materials as discussed above. The conclusion that f_u/f is a function of the stretch ratio had been reached independently by various authors.[31,33,42,54] The evidence for a dependence on the degree of cross-linking is scantier because of the lack of experimental data. A clear dependence is shown, however, for cross-linked polyethylene.

Our phenomenological theory can account for the observed behavior. We conclude that NR may not be the best material for testing the statistical theory through measurements of f_u/f. In terms of our theory this arises primarily from the weak dependence of n on T in this material over the range of temperature and cross-link density over which it has been investigated. We note that the stress–strain behavior of NR does not conform well to the predictions of the statistical theory either. By contrast cross-linked polystyrene or polyethylene with values of n close to 2 in the rubbery region would conform closely to the statistical theory in their stress–strain relations according to our theory but would, nevertheless, show dependence of f_u/f on λ and/or ν.

We have proposed a phenomenological theory which should allow extension of measurements of f_u/f to uncross-linked materials. This raises interesting possibilities. E.g., in styrene–butadiene gum stock $n \simeq 0.6$ and $dn/dT \simeq 0$. Thus, in light of our theory it should deviate strongly in its mechanical behavior from the equation

$$\sigma = G(\lambda - \lambda^{-2}) \tag{56}$$

but should show no dependence of f_u/f on λ.

Appendix

It is clearly important that the reference length L_0 should be defined in a consistent manner in deriving a set of interrelated data. Failure to do so can lead to appreciable error in f_u/f.

Let us consider a specimen subjected to a uniaxial stretch λ at temperature T and atmospheric pressure. Since $J \simeq 1$, eq 19 takes the form

$$f = 2GA_0(T)[\lambda^n - (J/\lambda)^{n/2}]/n\lambda \tag{A1}$$

$A_0(T)$ is the undeformed cross-sectional area at the temperature T. In force–temperature measurements at constant length

$$\lambda = \lambda^*/\lambda_0 = L(T)/L_0(T) \tag{A2}$$

where

$$\lambda^* = L(T)/L_0(T_0) \tag{A3}$$

and

$$\lambda_0 = L_0(T)/L_0(T_0) \tag{A4}$$

$L(T)$, $L_0(T)$, and $L_0(T_0)$ are the deformed length of the specimen at temperature T, the undeformed length at the same temperature, and undeformed length at the reference temperature T_0, respectively. The stretch ratio arising from the linear thermal expansion of the specimen from $L_0(T_0)$ to $L_0(T)$ is λ_0 and λ^* is the apparent stretch ratio referred to the undeformed length at T_0.

Let us denote the undeformed cross-sectional area at T_0 as $A_0(T_0)$. We then have

$$A_0(T) = A_0(T_0)\lambda_0^2 \tag{A5}$$

Substituting eq A2 through A5 into A1 we obtain

$$f = 2GA_0(T_0)\lambda_0^{3-n}[\lambda^{*n} - (J_0/\lambda^*)^{n/2}]/n\lambda^* \tag{A6}$$

where

$$J_0 = \frac{V(T)}{V_0(T_0)} = \lambda_0^3 J \simeq \lambda_0^3 \simeq 1 + 3\alpha_0(T - T_0) \tag{A7}$$

Equation A6 can be rewritten as

$$f = 2G^*A_0(T_0)[\lambda^{*n} - (J_0/\lambda^*)^{n/2}]/n\lambda^* \tag{A8}$$

where

$$G^* = GJ_0^{1-n/3} \tag{A9}$$

G^* is an apparent shear modulus defined in terms of λ^* instead of λ. Therefore, a change of the reference length from $L_0(T)$ to $L_0(T_0)$ changes the modulus but does not change the value of n. Furthermore, if $J \neq 1$, the restoring force f does not reduce to 0 when $\lambda^* \rightarrow 1$. Differentiation of eq A9 with respect to temperature leads to

$$\frac{\mathrm{d}G^*}{\mathrm{d}T} = J_0^{1-n/3}\frac{\mathrm{d}G}{\mathrm{d}T} + G(3 - n)\alpha_0 J_0^{-n/3} - [(G/3)J_0^{1-n/3}\ln J_0]\frac{\mathrm{d}n}{\mathrm{d}T} \tag{A10}$$

Equation A9 indicates that G^* does not differ too much from G. However, $\mathrm{d}G^*/\mathrm{d}T$ is quite different from $\mathrm{d}G/\mathrm{d}T$.

We illustrate this on data determined on natural rubber in our laboratory. With a reference temperature of 25 °C and a test temperature of 60 °C, $G = 6.22$ bar at the test temperature, $n = 1.64$, $\alpha_0 = 2.30 \times 10^{-4}$/°C, $\mathrm{d}G/\mathrm{d}T = 9.86 \times 10^{-3}$ bar/°C, we find $G^* = 6.33$ bar and $\mathrm{d}G^*/\mathrm{d}T = 12.78 \times 10^{-3}$ bar/°C, assuming that $\mathrm{d}n/\mathrm{d}T = 0$. Thus f_u/f at 60 °C calculated from $\mathrm{d}G^*/\mathrm{d}T$ is 0.090 lower than that calculated from $\mathrm{d}G/\mathrm{d}T$. It is clear that application of eq 9 and 34 requires very high precision in the determination of G. Thus, Shen and Blatz[25] have noted that specimen end effects can have a significant influence on f_u/f. As shown elsewhere[55] the ratio of free to bonded area in the specimen should be at least 50:1.

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(1) This work was supported by a grant from the National Science Foundation.
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