References and Notes

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The Elastic Restoring Force in Rubbers[1]

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ABSTRACT: The energetic and entropic contributions to the restoring force in natural rubber have been determined by measuring the force-temperature coefficient, the force-pressure coefficient, the isothermal compressibility, and the thermal expansion coefficient, all at constant length. The experimental results were compared with the predictions of several theories. Of these, an elastic potential function for compressible rubbers, recently developed by the authors, gave particularly satisfactory agreement. Published data on a chlorinated ethylene–propylene copolymer were used to show the applicability of the new potential function for predicting the internal energy contribution for the restoring force in rubberlike materials at high extensions.

The origin and experimental determination of the elastic restoring force in rubbers has been extensively studied. The subject has been reviewed in several recent publications.[3-5] In this paper we present thermoelastic measurements on natural rubber and correlate the data using an equation of state which is based on a new strain energy density function for compressible rubberlike materials.[6] Published data on a chlorinated ethylene–propylene copolymer rubber are used to demonstrate the use of the equation in predicting the relative contribution of internal energy to the restoring force at high elongations using only a few basic parameters.

The equation points out directions in which the statistical theory of rubber elasticity needs improvement.

Restoring Force

The elastic restoring force in rubbers results from deformational changes in the internal energy and the entropy of the rubber network. The internal energy changes are due to changes in the interchain and intrachain interactions in the network, whereas the entropy changes are associated with changes in the configurations of the network chains.

The elastic force f is the change in the Helmholtz free energy, A, with length in simple tension at constant temperature and volume. For derivation see, e.g., ref 7. Thus

$$f = \left.\frac{\partial A}{\partial L}\right|_{T,V} \qquad (1)$$

which, from the definition of the free energy may also be written as

$$f = \left.\frac{\partial U}{\partial L}\right|_{T,V} - T\left.\frac{\partial S}{\partial L}\right|_{T,V} \tag{2}$$

where U is the internal energy and S is the entropy.

The total force f is thus resolved into entropic and energetic components defined by

$$f_s \equiv -T\left.\frac{\partial S}{\partial L}\right|_{T,V} = T\left.\frac{\partial f}{\partial T}\right|_{V,L} \tag{3}$$

and

$$f_u \equiv \left.\frac{\partial U}{\partial L}\right|_{T,V} \tag{4}$$

The relative contribution of the internal energy to the elastic restoring force then results from eq 2 and 3 as

$$\frac{f_u}{f} = 1 - \frac{T}{f}\left.\frac{\partial f}{\partial T}\right|_{V,L} \tag{5}$$

Experimental determination of f_u/f thus requires measuring the changes in force with temperature at constant volume and length. The constant volume requirement necessitates the application of hydrostatic pressure during the measurement of the force-temperature coefficient. This experiment is extremely difficult to perform.[8,9] By a straightforward derivation (see, e.g., ref 7) it can be shown that

$$\frac{f_u}{f} = 1 - \frac{T}{f}\left.\frac{\partial f}{\partial T}\right|_{P,L} - \frac{T}{f}\gamma_{V,L}\left.\frac{\partial f}{\partial P}\right|_{T,L} \tag{6}$$

where the pressure-temperature coefficient at constant volume and length

$$\gamma_{V,L} = \left.\frac{\partial P}{\partial T}\right|_{V,L} = \beta_{P,L}/\kappa_{T,L} \tag{7}$$

is the ratio of the isobaric volumetric expansion coefficient, $\beta_{P,L}$, to the isothermal compressibility, $\kappa_{T,L}$, both at constant length. Thus, instead of measuring the force-temperature coefficient at constant volume and length, one may measure the force-temperature coefficient at constant pressure and length, if one determines, in addition, the force-pressure coefficient at constant temperature and length, the isobaric volumetric expansion coefficient, and the isothermal compressibility, both at constant length.

To circumvent the experimental difficulties inherent in using either eq 6 or 7, one often resorts to an elastic equation of state to replace one or the other term in eq 6 by an equivalent expression calculated from the equation. This procedure is subject to the validity of the assumptions made for the chosen equation of state and, thus, may be limited by the range within which the equation applies. Recently, Mark[5] has reviewed the published data of f_u/f for a large number of elastomers. In published works excepting that of Allen et al.[8,9] and that of Göritz and Müller[10] different equations of state were applied to estimate f_u/f. Allen et al. used eq 5 and 6 whereas Göritz and Müller employed calorimetric measurements. We have also used eq 6 although our experimental procedure differs in detail from that of Allen et al.[9]

Sample Preparation

Natural rubber samples were prepared from a rubber latex using the formula: Firestone S-5 Hevea Latex 100.0 parts, AZ-64 16.78 parts, Setsit-5 1.5 parts. AZ-64 is an aqueous dispersion prepared by Aztec Chemical Division of American Mineral Spirits Co., Los Angeles, Calif. When the amount shown is added to the latex, the mixture contains five parts of zinc oxide, two parts of sulfur, and two parts of Wingstay-L antioxidant per hundred parts of rubber. The latex and the dispersion were stirred for about 15 min and the slurrylike mixture was dried under vacuum for 2 days. Setsit-5, supplied by Vanderbilt Chemical Corp., Bethel, Conn., served as an accelerator. It was milled into the dry mixture which was cured in the mold for 8 h at 95 °C under a pressure of about 1750 bar (25 000 psi). Sheets 0.445 cm (0.175 in.) thick and 11.24 cm (6 in.) long and wide were obtained. The density of the rubber at 23 °C was 0.921 g/cm^3.

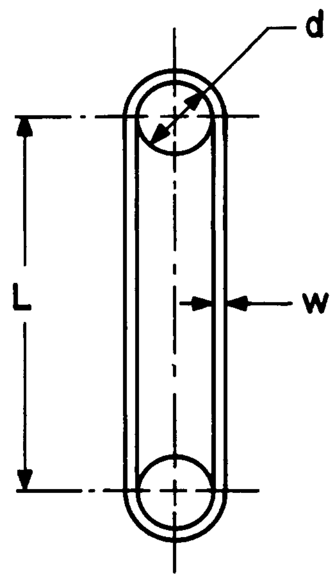

Figure 1. Ring specimen.

Specimens

The measurements were made on ring specimens of 3.81 cm (1.5 in.) outer and 3.43 cm (1.35 in.) inner diameter cut from the sheets using a double-bladed flycutter. During the cutting operation the rubber sheets were secured to a polyethylene backing sheet with double-sided adhesive tape.

At any extension the shape of the deformed ring is as shown in Figure 1. Here, L represents the separation of two hooks holding the sample and d is the diameter of these hooks. Most of the data will be presented in terms of the stress, σ, based on the undeformed cross-section of the ring at the reference temperature. This is thus given by

$$\sigma = f/2t_0w_0 \tag{8}$$

where f is the observed force, at the test temperature, and t_0 and w_0 are the initial thickness and width, respectively, both at the reference temperature. Thus, whenever σ will be used later, the equations are valid at the temperature of the reference state. When desired, these equations can easily be rewritten in terms of the force, $f = 2\sigma t_0 w_0$. The average extension ratio is given by

$$\lambda_{av} = c/c_0 \tag{9}$$

where c and c_0 are the average circumferences of the deformed and the undeformed ring, at the reference temperature, respectively. From inspection of the figure,

$$c = 2L + \pi(d + w) \tag{10}$$

and

$$c_0 = \pi D_a \tag{11}$$

Thus,

$$\lambda_{av} = [2L + \pi(d + w)]/\pi D_a \tag{12}$$

where D_a is the average diameter of the ring and w is the width of the deformed specimen at the test temperature. In practice, it is not always possible to measure the width of the deformed sample. One may then resort to the assumption of incompressibility to obtain an expression for w. We used eq 12 since we measured w as explained below. The stretch ratio, λ, referred to in the remainder of the text denotes the average value given by eq 12.

Force-Temperature Coefficient

The changes in force with temperature at various elongations were measured to obtain the force-temperature coefficient. The ring specimen was stretched to the desired elongation at room temperature in an Instron testing machine. The initial force was allowed to come to an equilibrium value and was then suppressed electronically to make it possible to observe the changes in the force resulting from changes in temperature on a more sensitive scale. To begin measurements, the temperature was raised to 60 °C and the force was again allowed to relax. The temperature was then lowered in steps of 10 °C and the relaxed force was recorded at each temperature. This procedure was repeated at various elongations, in both cooling and heating cycles. In general, it took 2 to 3 h for the force to become sensibly constant at a given temperature. The variation of this (near) equilibrium force with temperature was linear for a given extension ratio. The results are listed in column 3 of Table I in the form of $T\partial\sigma/\sigma\partial T$ at atmospheric pressure and constant length. The first two columns contain the (average) stretch ratio calculated from eq 12 and the stress at the reference temperature, calculated from eq 8, respectively. The very slight changes in the (average) length of the specimen, caused by the expansion or contraction of the rubber with temperature, were deemed negligible.

Force-Pressure Coefficient

The force-pressure coefficient at constant length was determined in a specially constructed apparatus which was described elsewhere.[11] The apparatus consists of a tensile tester inside a chamber which can be brought to about 138 bar (2000 psi) maximum pressure using silicone oil as the pressurizing fluid. The silicone oil did not appear to affect the measurements. Changes in force with pressure are roughly two orders of magnitude smaller than changes in force with temperature. The signal from the load cell of the tensile tester was therefore amplified by a transducer-amplifier fitted with a suppression module which allowed suppression of the initial value of the force to increase the sensitivity of the measurements.

Before conducting the force-pressure experiments the effect of pressure on the various measuring devices in the pressure chamber was determined. No effect of pressure on the thermocouple readings was found at the pressures employed. The output from the load cell showed good linearity, reproducibility, and no drift. The zero shift of the load cell due to the applied hydrostatic pressure was small, but not negligible. A small correction was substracted from the observed load.

The force-pressure coefficient was determined according to the following procedure. A ring specimen was pulled to the highest extension ratio to be used and allowed to stand for over a week at room temperature and atmospheric pressure. This provided sufficient time for the initial load to relax to an equilibrium value. The system was then pressurized to 138 bars and the temperature in the pressure chamber was brought to 25 °C. The system was maintained at this temperature and pressure until the force remained constant, at which time the load was recorded and then suppressed. The pressure was then decreased, usually in steps of 34.5 bars (500 psi). At each pressure the temperature was closely controlled at 25 °C and the force was allowed to come to equilibrium. In general the procedure took about 2 h at each pressure. It was not found necessary to repeat the experiment for increasing pressures since the force value could be checked from time to time for an intermediate pressure.

Table I
Relative Internal Energy Contribution to the Restoring Force in Natural Rubber at 25 °C as a Function of the Stretch Ratio

λ	σ, bar	$\left.\frac{T}{\sigma}\frac{\partial\sigma}{\partial T}\right\|_{P,L}$	$\left.\frac{T}{\sigma}\frac{\partial\sigma}{\partial P}\right\|_{T,L}$, K/bar × 10^2	f_u/f	f_u/f $(\text{BST})^2$	f_u/f (FCH)
1.250	3.228	0.460	2.81	0.23	0.27	0.32
1.491	5.225	0.596	1.50	0.24	0.26	0.31
1.713	7.426	0.624	0.959	0.27	0.27	0.33
1.776	7.961	0.648	0.868	0.26	0.26	0.31
1.925	9.105	0.700	0.750	0.22	0.22	0.27
2.300	10.600	0.724	0.621	0.21	0.21	0.26
2.586	11.880	0.735	0.552	0.21	0.21	0.25
3.083	13.720	0.760	0.482	0.19	0.18	0.22

After the force-pressure experiment was completed at one extension ratio, the ring specimen was brought to a lower extension and the procedure was repeated. The results of the measurements are tabulated in column 4 of Table I in the form of $T\partial\sigma/\sigma\partial P$ at constant temperature and length. We note that $\partial\sigma/\sigma\partial x = \partial f/f\partial x$, so that the entries in columns 3 and 4 of Table I represent the (normalized) force derivatives.

Pressure-Temperature Coefficient

Two experimental procedures for determining the pressure-temperature coefficient have been described in the literature. Allen et al.[8,9] calculated $\gamma_{V,L}$ from the ratio of $\beta_{P,L}$ to $\kappa_{T,L}$ which were determined in a special dilatometer. Bianchi and Pedemonte[12] estimated the pressure-temperature coefficient from measurements of the internal pressure. We employed an entirely different technique in which we measured the width of the specimen as a function of temperature and pressure at constant length using a highly sensitive displacement sensor based on the Hall effect. The theory of the sensor and experimental details were presented elsewhere.[13] We calculated $\gamma_{V,L}$ from the width-temperature and width-pressure coefficients, both at constant lengths, using the relation

$$\gamma_{V,L} = -\left.\frac{\partial w}{\partial T}\right|_{P,L} \Big/ \left.\frac{\partial w}{\partial P}\right|_{T,L} \tag{13}$$

To measure the width of the specimen the sensor is placed across its width. The two opposing surfaces of the specimen are in contact with a permanent magnet on one side and the Hall plate on the other.[13] The Hall plate senses the magnetic induction generated by the magnet across the specimen. Keeping the current constant, the changes in the width of the specimen are reflected in the changes of the Hall output voltage. The latter is calibrated as a function of the separation between the Hall Plate and the magnet using standard calibration gauges.

To measure the change in width with temperature as a function of elongation, a ring specimen was pulled to the highest extension ($\lambda \simeq 3$) and the sensor was placed across its width. The temperature inside the chamber was brought to 60 °C and the initial Hall output voltage was recorded and then suppressed. The temperature was now lowered to 0 °C in steps of 10 °C and the output voltage was recorded at each temperature. The output remained constant after a waiting period of 10 to 15 min at each temperature.

Having completed the measurements at one extension ratio, the specimen was brought to a lower extension and the procedure was repeated. The width-temperature coefficient at

Table II
Width-Temperature and Width-Pressure Coefficients as Functions of the Stretch Ratio

λ	$\frac{1}{w}\frac{\partial w}{\partial T}\Big\vert_{P,L}$, $\mathrm{K}^{-1} \times 10^4$	λ	$-\frac{1}{w}\frac{\partial w}{\partial P}\Big\vert_{T,L}$, $\mathrm{bar}^{-1} \times 10^6$
1.094	3.45		
1.252	3.53	1.276	32.3
1.501	3.51	1.535	31.3
1.746	3.54	1.792	31.9
1.996	3.44	2.051	31.6
2.242	3.46	2.312	31.7
2.490	3.45	2.573	31.3
2.736	3.43	2.836	32.9
2.983	3.53	3.097	32.8
Mean	3.48	Mean	32.0
SD	0.044	SD	0.63

a given stretch ratio is the slope of the (linear) width-temperature plot at the given elongation. The values of the coefficient as function of the stretch ratio are tabulated in Table II.

A similar procedure was followed to measure the changes in width with pressure. The Hall voltage was recorded as a function of pressure at various elongations, while the temperature of the pressure chamber was maintained at 25 °C. The width-pressure coefficients are also presented in Table II. Both the width-pressure and the width-temperature coefficients at constant length are independent of the strain in the range of extensions given in Table II. We note that these measurements can be made concurrently with the determinations of the force-temperature and the force-pressure coefficients, respectively.

The pressure-temperature coefficient at constant length is obtained from eq 13. This yields an average value of $\gamma_{V,L}$ = 10.9 bar/°C for our natural rubber sample over the range of extensions studied (i.e., up to $\lambda = 3$). The data tabulated in Table II support the contention of Flory[14] that the ratio of the expansion coefficient to the isothermal compressibility of amorphous cross-linked polymers should be independent of strain. This result is also in agreement with the dilatometric data of Allen et al.[6,7] who observed the same strain independence up to an extension of about 2.0.

Results

From the value of $\gamma_{V,L}$ and the data tabulated in columns 3 and 4 of Table I we calculated f_u/f as a function of λ using eq 6. The values are listed in the last column of Table I. We also calculated the stress, σ, and its energetic component, σ_u. The entropic component, σ_s, was obtained by difference. The quantities σ, σ_s, and σ_u are ploted as functions of λ in Figure 2. All three quantities represent the force referred to the undeformed area at the reference temperature, 25 °C. The circles and squares on the σ curve represent the stresses measured in the experiments in which the stress-temperature and the stress-pressure coefficient, respectively, were determined.

Evidently, most of the restoring force in natural rubber has its origin in entropy changes, but a significant part comes from changes in the internal energy. The data indicate that the relative internal energy is, within the limits of the experimental error, a constant independent of the strain at stretch ratios below 3. The mean value for our natural rubber sample in this region is 0.23, with a standard deviation of 0.027. We note that this value was obtained purely from thermodynamic measurements, without recourse to any constitutive equation.

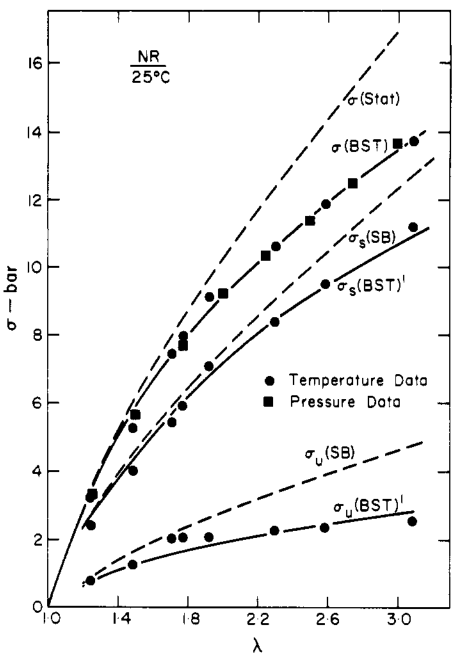

Figure 2. Comparison of experimental data with the predictions of the theories of Shen and Blatz and of Sharda and Tschoegl.

We have recently reported on a strain energy density function for compressible rubberlike materials.[6] This is a modification of the elastic potential function of Blatz, Sharda, and Tschoegl for incompressible rubberlike materials, which[15] we shall refer to as the BST potential for shortness. The single-term form of our modification which is valid for stretch ratios less than about 3 gives the force in simple tension as

$$f = (2G/n)A_0J^{\gamma}[\lambda^{n-1} - J^{n/2}/\lambda^{(n+2)/2}] \qquad (14)$$

where G is the shear modulus, A_0 is the undeformed area, J ($=V/V_0$) is the ratio of the deformed to the undeformed volume, the exponent γ accounts for the slight volume dependence of the shear modulus,[16] and the exponent n is a material parameter which we have earlier shown[15] to be 1.64 for natural rubber. The exponent γ is obtained from the force-pressure coefficient as a function of the stretch ratio as explained in our earlier paper.[6] The value we found for our natural rubber sample was $\gamma = -0.18$.

We may use eq 14 in conjunction with eq 5 to predict the relative internal energy contribution to the restoring force. For the following analysis it is assumed that γ and n are independent of temperature and pressure, at least in the small range of temperature and pressure we will consider in this work. For n this assumption is supported by experimental evidence.[15]

According to eq 14 the temperature derivative of the force at constant V and L is

$$\frac{\partial \ln f}{\partial T}\Big\vert_{V,L} = \frac{1}{G}\frac{\mathrm{d}G}{\mathrm{d}T} + \alpha_0(3 - n - 3\gamma) \qquad (15)$$

keeping in mind that V_0, A_0, and L_0 change with temperature. In eq 15 α_0 is the linear expansion coefficient of the undeformed material. This is two thirds of the (average) value of $\partial \ln w/\partial T$ (see Table II), because the latter is at constant length. Thus, $\alpha_0 = 2.32 \times 10^{-4}\ \mathrm{K}^{-1}$. From eq 5 and 15

$$\frac{f_u}{f}(\mathrm{BST})^1 = 1 - \frac{T}{G}\frac{\mathrm{d}G}{\mathrm{d}T} - \alpha_0T(3 - n - 3\gamma) \qquad (16)$$

where the letters BST identify it as being derived from our modification of the BST potential and the superscript 1 distinguishes this expression from one to be derived below.

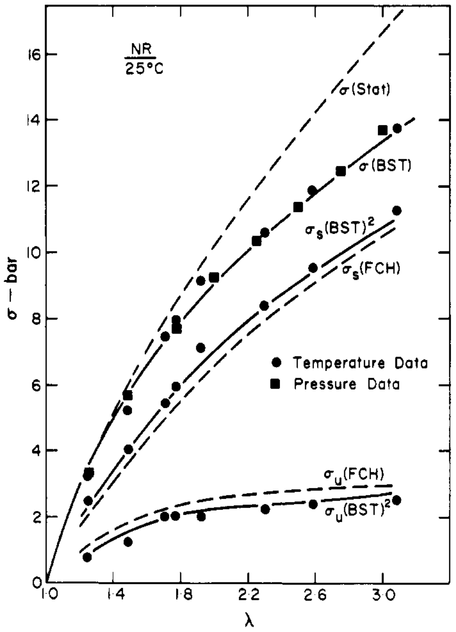

Figure 3. Comparison of experimental data with the predictions of the theories of Flory, Ciferri, and Hoeve and of Sharda and Tschoegl.

Now $J \simeq 1$ and we may, therefore, obtain the stress referred to the cross-sectional area at the reference temperature from eq 14 as

$$\sigma(\mathrm{BST}) = (2G/n)[\lambda^{n-1} - 1/\lambda^{(n+2)/2}] \tag{17}$$

which is the equation of Blatz, Sharda, and Tschoegl.[15] Decomposing this into the energetic and entropic components gives

$$\sigma_{\mathrm{u}}(\mathrm{BST})^1 = \sigma(\mathrm{BST})\left[1 - \frac{T}{G}\frac{\mathrm{d}G}{\mathrm{d}T} - \alpha_0 T(3 - n - 3\gamma)\right] \tag{18}$$

and

$$\sigma_{\mathrm{s}}(\mathrm{BST})^1 = \sigma(\mathrm{BST})\left[\frac{T}{G}\frac{\mathrm{d}G}{\mathrm{d}T} + \alpha_0 T(3 - n - 3\gamma)\right] \tag{19}$$

We obtained G from eq 17 as 5.87 bar at 25 °C. The derivative, d ln G/d ln T, cannot be obtained with a precision better than ±5%. We therefore used the value within this range which best fitted the data. This value was 0.66. The solid lines in Figure 2 represent eq 17, 18, and 19. The fit is very satisfactory. The value of f_{u}/f found from eq 16 is 0.21.

An alternative expression for f_{u}/f may be obtained by considering the temperature derivative of the force at constant P and L, which is

$$\left.\frac{\partial \ln f}{\partial T}\right|_{P,L} = \frac{1}{G}\frac{\mathrm{d}G}{\mathrm{d}T} + \alpha_0\left[\frac{(3 - n)\lambda^{3n/2} - (3 + n/2)}{\lambda^{3n/2} - 1}\right] \tag{20}$$

where we used the fact that $\beta_{P,L} = 3\alpha_0$ because the volume expansion remains the same whether or not one of the lengths is fixed. Eliminating d ln G/d ln T between eq 16 and 20 yields

$$\frac{f_{\mathrm{u}}}{f}(\mathrm{BST})^2 = 1 - \left.\frac{T}{f}\frac{\partial f}{\partial T}\right|_{P,L} - \left[\frac{n}{2(\lambda^{3n/2} - 1)} - \gamma\right]3\alpha_0 T \tag{21}$$

and decomposition into the energetic and entropic components gives

$$\sigma_{\mathrm{u}}(\mathrm{BST})^2 = \sigma(\mathrm{BST})\left\{1 - \left.\frac{T}{f}\frac{\partial f}{\partial T}\right|_{P,L} - \left[\frac{n}{2(\lambda^{3n/2} - 1)} - \gamma\right]3\alpha_0 T\right\} \tag{22}$$

and

$$\sigma_{\mathrm{s}}(\mathrm{BST})^2 = \sigma(\mathrm{BST})\left\{\left.\frac{T}{f}\frac{\partial f}{\partial T}\right|_{P,L} - \left[\frac{n}{2(\lambda^{3n/2} - 1)} - \gamma\right]3\alpha_0 T\right\} \tag{23}$$

Equations 22 and 23 are represented by the solid lines in Figure 3. Again the fit is excellent. Contrary to eq 16, eq 21 contains the stretch ratio, λ, explicitly. The dependence on the stretch ratio is largely compensated for by the force-pressure term.

Table III
Relative Internal Energy Contribution to the Restoring Force in Natural Rubber[a]

Method	f_{u}/f Mean	f_{u}/f SD	Eq
Thermodynamic	0.23	0.027	6
BST[1]	0.21		16
Shen and Blatz	0.27		25
BST[2]	0.24	0.034	21
Flory et al.	0.28	0.039	26

[a] Comparison of thermodynamic measurements with different predictions.

The values of f_{u}/f calculated from eq 21 are tabulated in column 6 of Table I. Their mean value is 0.24 with a standard deviation of 0.034. There appears to be a slight dependence of f_{u}/f on λ but this may well be within the experimental error.

We note that the predictions of our theory reduce to those of the statistical theory of rubber elasticity for $n = 2$ and $\gamma = 0$. We have

$$\sigma(\mathrm{STAT}) = G(\lambda - \lambda^{-2}) \tag{24}$$

for the total stress, while eq 16 and 21 yield

$$\frac{f_{\mathrm{u}}}{f}(\mathrm{SB}) = 1 - \frac{T}{G}\frac{\mathrm{d}G}{\mathrm{d}T} - \alpha_0 T \tag{25}$$

and

$$\frac{f_{\mathrm{u}}}{f}(\mathrm{FCH}) = 1 - \left.\frac{T}{f}\frac{\partial f}{\partial T}\right|_{P,L} - \frac{3\alpha_0 T}{\lambda^3 - 1} \tag{26}$$

for the relative internal energy contribution. In these equations SB stands for Shen and Blatz[17] and FCH stands for Flory, Ciferri and Hoeve[18] who first derived these equations. The energy-elastic and entropy-elastic components of the stress become

$$\sigma_{\mathrm{u}}(\mathrm{SB}) = G(\lambda - \lambda^{-2})\left(1 - \frac{T}{G}\frac{\mathrm{d}G}{\mathrm{d}T} - \alpha_0 T\right) \tag{27}$$

and

$$\sigma_{\mathrm{s}}(\mathrm{SB}) = G(\lambda - \lambda^{-2})\left(\frac{T}{G}\frac{\mathrm{d}G}{\mathrm{d}T} + \alpha_0 T\right) \tag{28}$$

according to Shen and Blatz, and

$$\sigma_{\mathrm{u}}(\mathrm{FCH}) = G(\lambda - \lambda^{-2})\left[1 - \left.\frac{T}{f}\frac{\partial f}{\partial T}\right|_{P,L} - \frac{3\alpha_0 T}{\lambda^3 - 1}\right] \tag{29}$$

and

$$\sigma_s(\text{fch}) = G(\lambda - \lambda^{-2}) \left[\frac{T}{f}\frac{\partial f}{\partial T}\bigg|_{P,L} - \frac{3\alpha T}{\lambda^3 - 1}\right] \qquad (30)$$

according to Flory et al., respectively. The predictions provided by eq 24, 27, and 28 and by eq 24, 29, and 30 are plotted in Figures 2 and 3, respectively, for comparison. The values of f_u/f calculated from eq 25 and 26 were 0.27 and 0.28, respectively, the latter with a standard derivation of 0.039. These results are summarized in Table III.

Discussion

The only published data that are strictly comparable with our thermodynamic measurements based on eq 6 are the data by Allen, Kirkham, Padget, and Price.[9] The calorimetric data of Göritz and Müller[10] give 0.35 for f_u/f at 44 °C, below $\lambda = 3$. All other literature values are based on eq 25 or 26 or a variant thereof. Allen et al. examined five natural rubber samples. These were prepared from smoked sheet and cured with dicumyl peroxide. Their moduli (calculated from the Mooney–Rivlin constants) varied from 1.70 to 4.58 bar. The mean value of f_u/f for the five samples was 0.13, considerably lower than our value of 0.23. Their and our samples differed in other respects also. While we found $\beta_{P,L}$ and $\gamma_{V,L}$ to be 6.96×10^{-4} K^{-1} and 10.9 bar/K, respectively, for our sample, Allen et al. found 6.98×10^{-4} K^{-1} (at 25 °C) and 11.8 bar/K, respectively, for theirs. There were differences in the mode of measurement also. We used ring specimens while Allen et al. employed strips. Their measurements of $\beta_{P,L}$ and $\gamma_{V,L}$ were made dilatometrically, ours were based on the measurement of thickness changes.

In a recent paper Wolf and Allen[19] reconsidered earlier data of Allen and his co-workers and concluded the most reliable value for f_u/f from their work to be 0.18. The scatter in the determination of f_u/f values is generally high as shown in Figure 4 which contains plots of f_u/f as a function of λ from our own work as well as that of Shen, McQuarrie, and Jackson,[20] Roe and Krigbaum,[21] Shen and Blatz,[17] Allen, Bianchi, and Price,[8] Allen, Kirkham, Padget, and Price,[9] and Smith, Greene, and Ciferri.[22] With the exception of ours and the data of Allen, Kirkham, Padget, and Price, the f_u/f values were calculated from eq 26.

Figure 4 shows three distinct regions of f_u/f values for natural rubber. In the region of small strains ($\lambda < 1.2$) f_u/f appears to be a function of λ; in the region of moderate strains ($1.2 < \lambda < 3.0$) f_u/f is sensibly independent of λ; at large strains ($\lambda > 3.0$) f_u/f definitely depends on the stretch ratio. The data in the small strain region do not agree with the predictions of either eq 16 or 25, which we believe to be more likely to be correct in this region. In the region of small strains eq 21 and 26 require extremely precise values of the force and the stretch ratio because of the appearance of the differences, $\lambda^3 - 1$ and $\lambda^{3n/2} - 1$, in the denominators of the second and third terms, respectively. As these differences approach zero, the force, f, diverges. Thus, the value of f_u (and, therefore, f_s) at $\lambda = 1$ cannot be obtained by extrapolation of data in the small strain region from either equation. Thus, in this region, eq 16 and 25 appear preferable. According to these equations, f_u/f is not a function of λ. Unfortunately, the determination of a reliable value of d ln G/d ln T (eq 16 and 25) also requires extremely precise measurements.

Figures 2 and 3 clearly show that the statistical theory does not predict the observed behavior beyond about 40% strain, whereas eq 16 and 21 do an excellent job over the entire range studied. As shown in Table III the predictions of eq 16 and 21 agree within the experimental error with our measurements based on eq 6. The predictions of eq 25 and 26, which are both based on the statistical theory of rubber elasticity, agree well with each other, but not with our experimental value. The difference of about 0.04 arises primarily from the neglect of the volume dependence of the modulus in the statistical theory. It is thus seen that introduction of the parameter γ into the strain energy density function provides an important degree of freedom in accounting for interchain interaction effects. The rather small contribution which this term makes to f_u/f suggests that the contribution of the interchain interactions is quite small compared to the other components which make up the contribution of the internal energy to the restoring force.

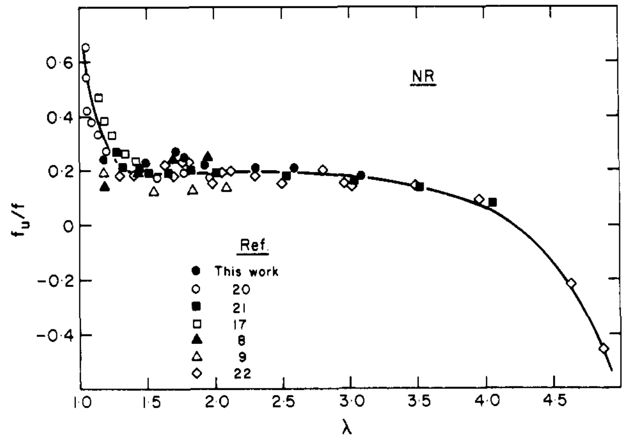

Figure 4. Plots of f_u/f vs. λ for natural rubber.

Our experimental data also explain why eq 26, which is based o the statistical theory, yields good values for f_u/f at strains where the statistical theory does not describe the deformation behavior. From the results in Table I we conclude that the force-pressure term in eq 6 becomes smaller as the strain increases, and f_u/f is well approximated by the simple relation

$$\frac{f_u}{f} \simeq 1 - \frac{T}{f}\frac{\partial f}{\partial T}\bigg|_{L,P} \qquad (31)$$

at large values of λ. Both eq 26 and 21 reduce to eq 31 in the limit of large values of the stretch ratio. Thus, it is not surprising that these equations describe the f_u/f data quite well. It is clear, however, that they must be handled with caution. If the purpose is to obtain f_u/f values at large values of λ, they provide excellent results. For the comparison of theories they are less well suited. They estimate only the last term of the thermodynamic equation since they share with it the numerically larger second term containing the experimentally determined quantity $(\partial \ln f/\partial \ln t)_{P,L}$. The comparison is particularly poor at moderate-to-large values of λ because the last terms in both equations rapidly decrease as λ increases.

Equations 16 and 25 imply that f_u/f is independent of strain. This is true for eq 25 over the entire range of strain and for eq 16 up to the point ($\lambda \simeq 3$) where the parameters n and G adequately describe the deformation behavior, provided always that the strain parameter n is, in fact, independent of the temperature. As will be shown in the next section, the theory of Sharda and Tschoegl[6] predicts f_u/f to be strain dependent beyond this point. The dependence of f_u/f on strain had been predicted earlier by Roe and Krigbaum[21] and by Shen.[23]

Chlorinated EPR. In the case of natural rubber, only one term in the strain energy density functions was necessary for an adequate representation of the data since these did not exceed 200% strain. To check the applicability of the two-term potential,[15] we examined the data of Natta, Crespi, and Flisi,[24] on chlorinated ethylene–propylene rubber (EPR). These data extend to a stretch ratio of nearly 7.

The two-term equation corresponding to eq 16 is

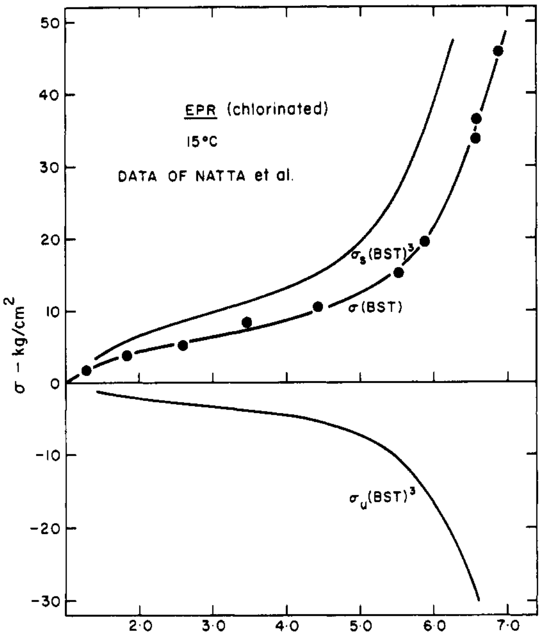

Figure 5. Plots of stress and its entropic and energetic components for chlorinated EPR. Data of Natta et al.[23]

$$(f_u/f)(BST)^3 = 1 - (3 - n - 3\gamma)\alpha_0 T - \frac{\dfrac{2T}{n}\dfrac{dG}{dT} + mT\dfrac{dB}{dT}{I_E}^{m-1} - m(m-1)B\alpha_0 {I_E}^{m-2}(\lambda^n + 2\lambda^{-n/2})}{2G/n + mB{I_E}^{m-1}} \qquad (32)$$

Equation 32 is obtained[6] from the two-term analogue of eq 14

$$f = (2G/n + mB{I_E}^{m-1})A_0 J^\gamma[\lambda^{n-1} - J^{n/2}/\lambda^{(n+2)/2}] \qquad (33)$$

and from that of eq 20

$$\left.\frac{\partial \ln f}{\partial T}\right|_{P,L} = \frac{(2/n)(dG/dT) + m(dB/dT){I_E}^{m-1} - m(m-1)B{I_E}^{m-2}\alpha_0(\lambda^n - \lambda^{-n/2})}{2G/n + mB{I_E}^{m-1}} + \alpha_0\frac{(3-n)\lambda^{3n/2} - (3 + n/2)}{\lambda^{3n/2} - 1} \qquad (34)$$

In these equations

$$I_E = (2\lambda^n + \lambda^{-2n} - 3)/n \qquad (35)$$

The data of Natta et al. are plotted in Figure 5. The solid line through the experimental points represents the least-squares fit with the parameters $n = 1.71$, $m = 4.84$, $B = 6.47 \times 10^{-5}$ kg/cm^2, and $G = 2.71$ kg/cm^2. These parameters were then used in eq 34 to predict the stress-temperature slopes shown in Figure 6. The values of dG/dT and dB/dT were 14.2×10^{-3} and 5.54×10^{-7} kg/(cm^2 °C), respectively, as found from the initial slopes of the stress–strain curves at different temperatures. Figures 5 and 6 indicate excellent agreement of eq 33 and 34 with the experimental data.

These parameters (with $\gamma = 0$) may then be used to predict f_u/f by eq 32. The results are shown in Figure 7. The components σ_u and σ_s are given in Figure 5. It is seen that for this rubber f_u/f is negative. It stays constant up to an extension ratio of about 3.0 and decreases beyond this point.

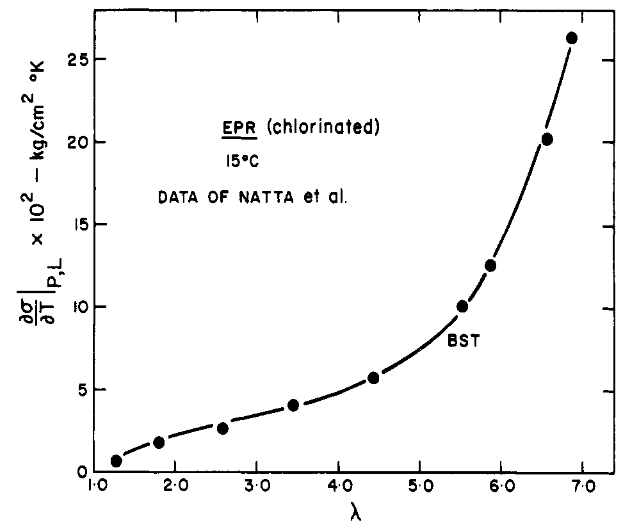

Figure 6. Stress-temperature coefficients for chlorinated EPR. Data of Natta et al.[23]

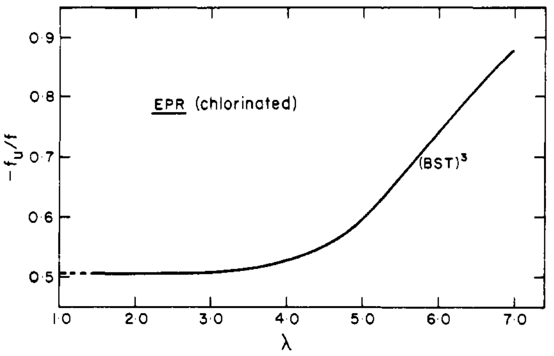

Figure 7. Plot of f_u/f vs. λ for chlorinated EPR.

Conclusion

The statistical theory is the only theory of rubber elasticity which is based on a molecular model. It is an isochoric theory. The work presented here shows (as does that presented in ref 6) that the theory requires extension to account for the small but not always negligible volume changes which may occur during deformation.

Our work also supports evidence given or discussed elsewhere[15,25,26] that the statistical theory does not correctly represent the stress–strain behavior in simple tension even below 40% strain for most materials.

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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