

Determination of Internal Energy Contribution to the Thermoelasticity of Natural Rubber During Compression by Use of a Thermomechanical Analyzer

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Synopsis

A method for measuring the internal energy change of elastomers under compression is demonstrated using a conventional thermomechanical analyzer. The method is rapid and convenient and has a major advantage in that only a very small sample is required. Results are reported for natural rubber cured with two different crosslinking agents. The results are compared with previous work on similar materials in tension and torsion.

INTRODUCTION

Reviews on the thermoelasticity of rubbery materials have been made recently by Shen et al.,¹ Treloar,^{2,3} Guth,⁴ and Tobolsky.⁵ It has been found that although a number of investigations have been conducted on samples in extension,⁶⁻⁴⁷ simple shear,⁴⁸ and torsion,^{2,49,50} studies on the thermoelastic properties of rubbery materials under compression are rare. The only published article we found for the compression case was a study of the thermoelasticity of a swollen styrene-divinylbenzene copolymer using a Höppler consistometer.⁵⁴

From the theory of rubber elasticity^{51,52} the equations are applicable

$$f = \left(\frac{\partial E}{\partial L} \right)_{T,V} + T \left(\frac{\partial f}{\partial T} \right)_{V,L} = f_e + T \left(\frac{\partial f}{\partial T} \right)_{L,V} \quad (1)$$

$$f = f_e + T \left(\frac{\partial f}{\partial T} \right)_{P,L} + T \left(\frac{\partial P}{\partial T} \right)_{V,L} \left(\frac{\partial f}{\partial P} \right)_{T,L} \quad (2)$$

equally to elongation or compression of a rubbery material.^{2,51} In these equations, f is the equilibrium stress at a given state of the system specified by a set of variables T, V, L or T, P, L ; E is the internal energy; f_e is the internal energy contribution to the equilibrium stress; V, T , and P are the volume, temperature, and external pressure of the sample; and L is the length of the sample at the equilibrium state. According to eq. (1), f_e can

be determined from the intercept of f versus T at constant volume. However, the achievement of the condition of constant volume requires the application of hydrostatic pressure during the thermoelastic measurements, and this is extremely difficult to do experimentally.^{12,18} The difficulty of obtaining $(\partial P/\partial T)_{V,L} - (\partial f/\partial P)_{T,L}$ still exists. Although f_e can also be obtained by eq. (2). Flory et al.^{26,53} and Shen et al.¹² have derived an equation for f_e from the statistical theory of rubber elasticity as follows:

$$f_e/f = 1 - (T/f) (\partial f/\partial T)_{P,L} - [\beta_v T/(\alpha^3 - 1)] \quad (3)$$

where β_v is the cubic thermal expansion coefficient of the sample, α is L/L_0 , and L_0 is the length of the unstressed sample at temperature T . Thus, f_e can be easily calculated from the measurement of f versus T at constant pressure. In addition, a rather simple equation for determining f_e was derived by Shen^{7,12} using eq. (3) and the statistical theory^{39,51} as follows:

$$f_e/f = 1 - \frac{T}{G} \frac{dG}{dT} - \frac{\beta_v T}{3} \quad (4)$$

where G is the shear modulus of the sample, i.e., the slope of f versus $\alpha - 1/\alpha^2$. The present work shows how f_e/f can be measured accurately and quickly from eq. (4) using a conventional thermomechanical analyzer, requiring only a small amount of sample.

EXPERIMENTAL

The two samples of natural rubber were kindly supplied by B. F. Goodrich Co., Avon Lake, Ohio and General Tire and Rubber Co., Akron, Ohio. Sample, A, from B. F. Goodrich, was crosslinked by 2.5 phr dicumyl peroxide and was cured 20 min at 320°F. Sample, B, from General Tire and Rubber Co., was crosslinked by sulfur and was cured 20–30 min at 287°F. Specimens were cut from the above samples using a paper punch with size approximately equal to the diameter of the probe of the du Pont 941 thermal-mechanical analyzer, TMA.⁵⁵ A du Pont Model 900 differential thermal analyzer was used as a control unit and readout for the TMA. A schematic description of the TMA is shown in Figure 1 of ref. 57. The probe used was a quartz rod, radius = 0.125 cm, with a flat end.

The calibration of the TMA was made using the known linear thermal expansion of aluminum and lead with the standard procedure in the operation manual. The thickness of the specimen was about 0.200 cm and the weight was ≈ 60 mg. The cut specimen was left at room temperature for one week to relax any stresses induced by cutting. The sample was placed under the end of the probe. The probe was adjusted to just touch the surface of the rubber, using the probe position controller. The temperature was increased at a heating rate of 5°C/min until a temperature of 80°C was reached. The slope of the probe displacement (calculated from the calibrated sensitivity of TMA) versus temperature was used to calculate the linear thermal expansion coefficient of the rubber, which was needed to calculate f_e/f by eq. (4).

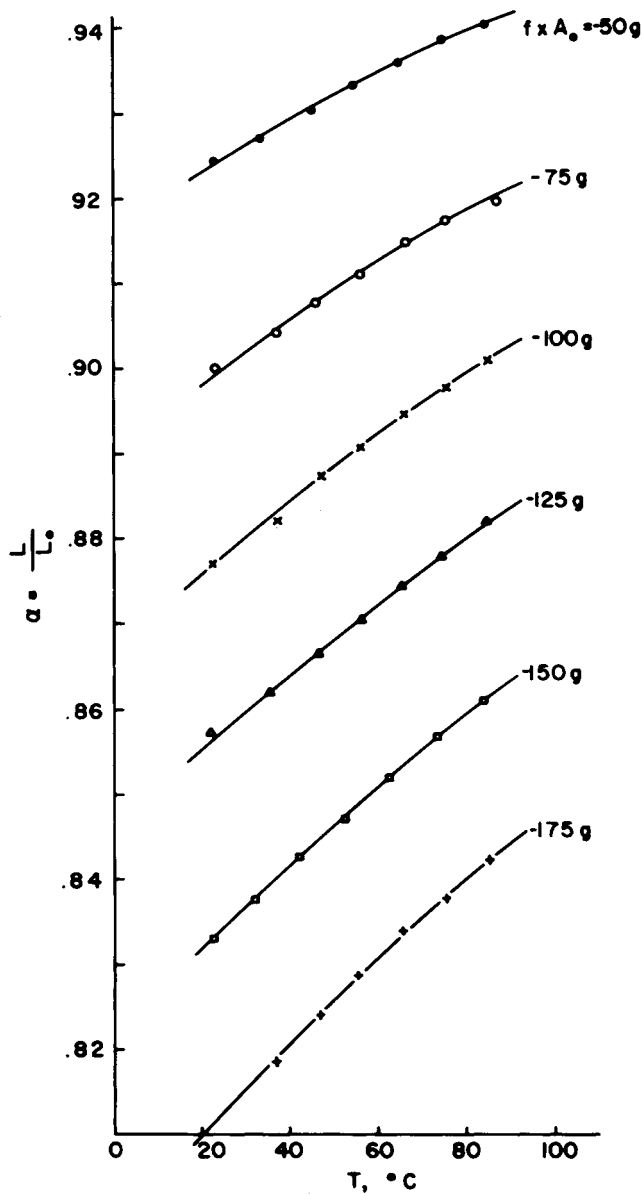


Fig. 1. Deformation ratio vs. temperature at constant force: sample A.

A load of constant weight was next applied to the probe for 64 hr at room temperature to attain a pseudo-equilibrium state.¹² The temperature was then increased, using $\sim 10^\circ\text{C}$ intervals, with at least 45 min between successive intervals. It was found that there was no detectable difference in the displacement between 45 min and 1 hr so that the 45-min displacement was treated as an equilibrium displacement. At room temperature, when the

load was removed the sample returned to within one percent of the original length; creep was not a significant factor. The displacement-temperature measurements were repeated at other levels of applied stress. Relaxation periods of at least 12 hr were given after each change in applied stress. Nitrogen was purged through the sample chamber to minimize oxidation.

RESULTS

Figures 1 and 2 show the data from these measurements at different compressive loads for samples A and B, respectively. In these figures the displacements and the sample lengths at the specific temperatures have been corrected for thermal expansion using the measured thermal expansion coefficients (2.45×10^{-4} cm/cm $^{\circ}\text{C}^{-1}$ for sample A and 2.30×10^{-4}

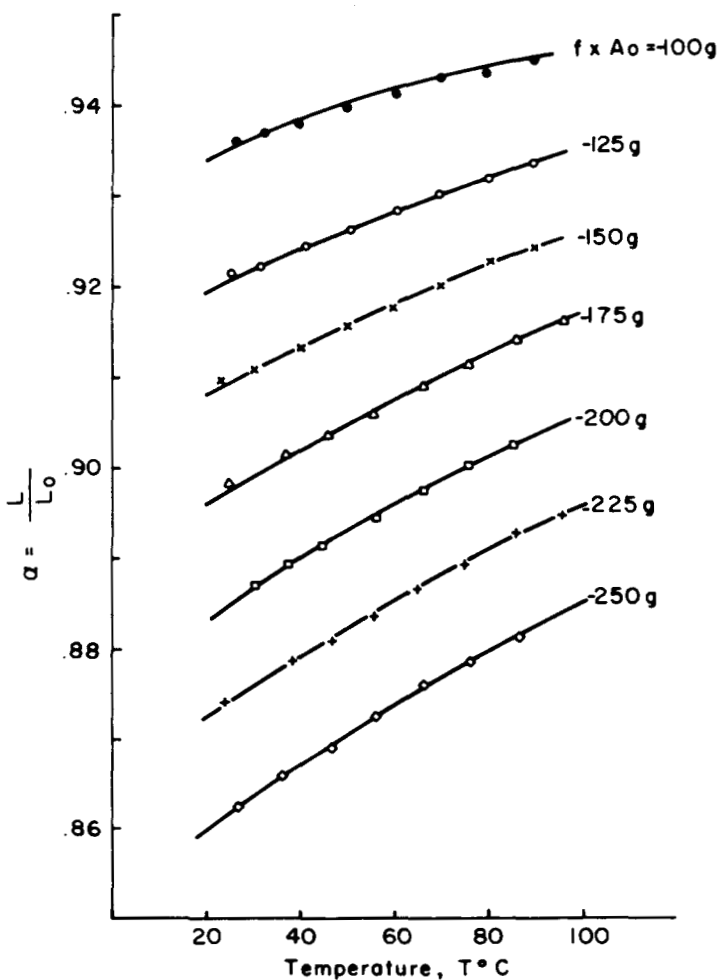


Fig. 2. Deformation ratio vs. temperature at constant force: sample B.

TABLE I
Comparison of Shear Modulus Measured by Different Methods

Methods	Shear modulus (at 25°C), megadynes/cm ²	Difference (based on compression data), %
Compression (TMA)	5.80	0
Simple tension (Instron)	5.51	5.00
Radius of contact (Wood ⁵⁸)	5.41 ^a	6.72
Indentation (Waters ⁶⁰)	5.46	5.86

^a At fraction of decomposition $F = 0.774$ (calculated according to eqs. (1) and (3) of ref. 59) and parts of dicumyl peroxide $P = 2.5$ phr.

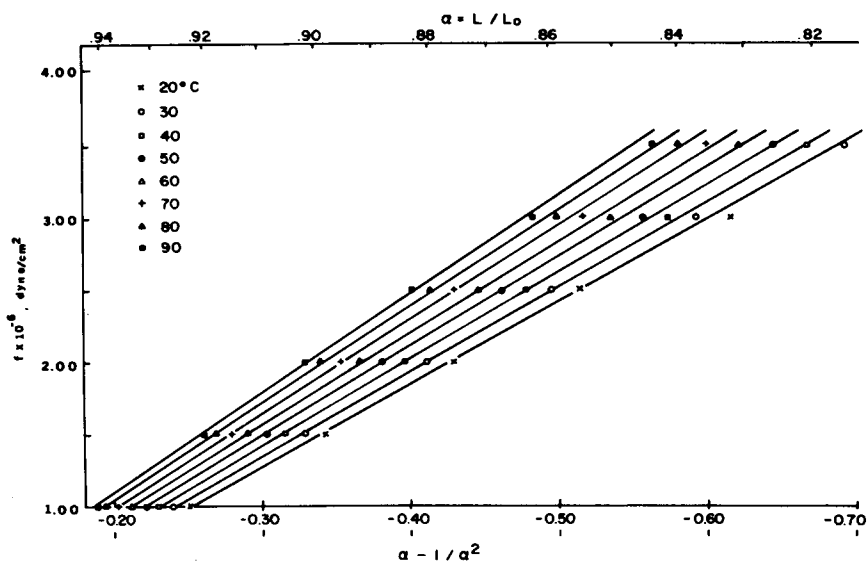


Fig. 3. Determination of shear modulus: sample A.

cm/cm °C⁻¹ for sample B). These values are somewhat higher than the 2.20×10^{-4} cm/cm °C⁻¹ previously reported,^{7,12,13,15,17,18} but the effect of this difference on the calculated values of f_e/f is less than 8% for sample A and 13% for sample B. The above linear expansion coefficient was taken equal to $\beta_v/3$ for calculating f_e/f .

Figures 3 and 4 show plots of compressive force f versus $\alpha - (1/\alpha^2)$ with temperature as a parameter from the data of Figures 1 and 2. According to the statistical theory,^{39,50,51} the slopes of f versus $\alpha - (1/\alpha^2)$ in Figures 3 and 4 give the shear moduli of the rubber specimens. The shear moduli were used to determine f_e/f , using eq. (4). The deviations from straight-line behavior in the plot of f versus $\alpha - (1/\alpha^2)$ at higher strain are due to the nonlinear behavior of rubber at high strain where the statistical theory becomes inadequate.¹² The shear modulus at 25°C was also calculated from Young's modulus measured with an Instron tensile tester, and it was

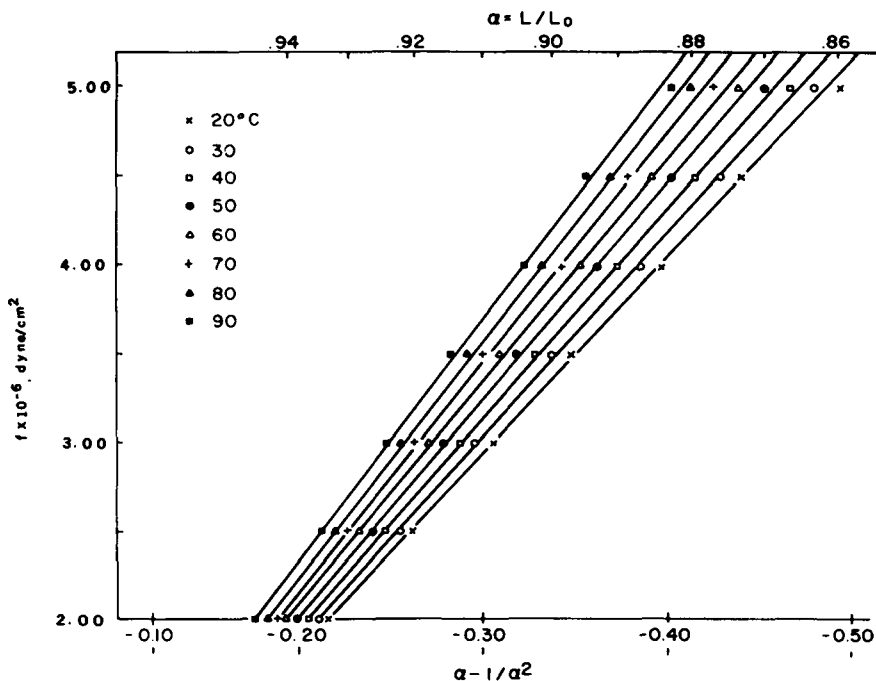


Fig. 4. Determination of shear modulus: sample B.

found that the value of shear modulus differed from this compression result by only 5.0%. The value of shear modulus has also been checked with Wood⁵⁸ and Waters⁶⁰ works, and the results are in good agreement (see Table I).

In order to calculate f_e/f from eq. (4), the dG/dT term was obtained from the slope of G -versus- T plots as shown in Figures 5 and 6. The linearity of G versus T is in agreement with the statistical theory,^{51,56} providing no significant change of density occurs within the low range of measuring temperatures, since

$$G = \frac{\rho RT}{M_c} (1 - 2M_c/\bar{M}_n) \quad (5)$$

where ρ is the density of polymer, R is the gas constant, M_c is the molecular weight between crosslinks, and \bar{M}_n is number-average molecular weight of the rubber. If the change in ρ is negligible, all other parameters except T are constant.

Values of f_e/f calculated from dG/dT and β_e at 30°C are 0.106 for sample A and 0.067 for sample B. Both these results are independent of strain. There is a temperature dependence due to the $\beta_e T/3$ term.

DISCUSSION

The thermoelasticity of natural rubber has been studied by numerous authors.^{6,7,12-18,20,26,27,30,34-39,44,45,47,49} Some authors^{14,15,20,30} have reported

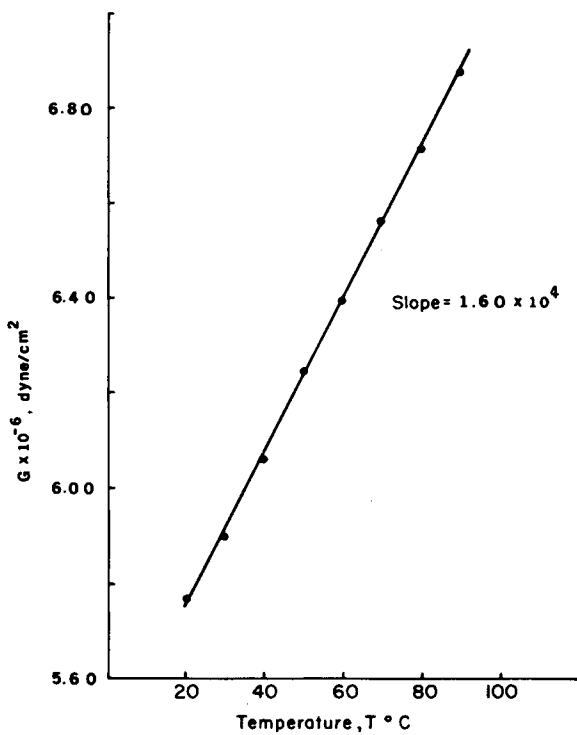


Fig. 5. Shear modulus vs. temperature: sample A.

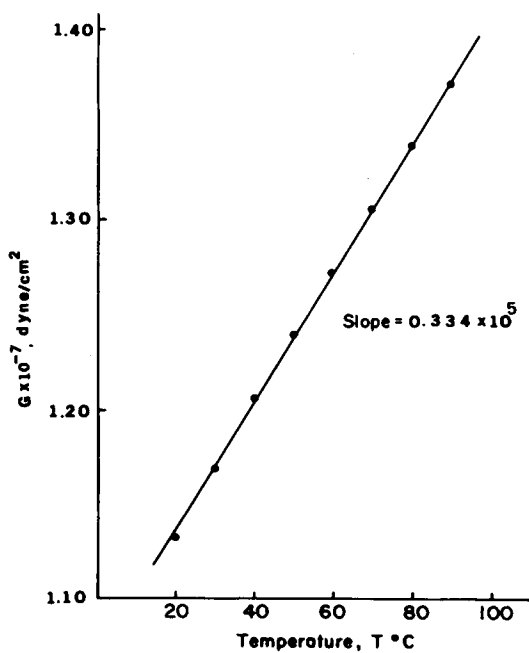


Fig. 6. Shear modulus vs. temperature: sample B.

TABLE II
 Values of f_e/f for Natural Rubber

f_e/f	Temperature, °C	Reference	Method of determination ^a	Crosslinking agent or method
0.106	30	this work	compression, const. P , eq. (4)	dicumyl peroxide
0.116	20	this work	compression, const. P , eq. (4)	dicumyl peroxide
0.126	20	Boyce et al. ⁴⁹	torsion, const. P	dicumyl peroxide
0.067	30	this work	compression, const. P , eq. (4)	sulfur
0.15	30	Shen et al. ¹²	tension, const. P , eq. (4)	dicumyl peroxide
0.17	30	Ciferri ¹⁶	tension, const. P , eq. (3)	γ -radiation
0.13	40	Ciferri et al. ²⁶	calculated from data by Wood et al. ²⁷	sulfur
0.20	45	Roe et al. ¹⁵	tension, const. P , eq. (3)	irradiation in N_2
0.125	40	Yamamoto et al. ³⁷	tension, const. P , eq. (3)	sulfur
0.10	50	Tanaka et al. ¹³	tension, const. P , eq. (3)	sulfur
0.20	30	Allen et al. ¹⁸	tension, const. V , eq. (1)	unknown
0.120	45	Allen et al. ¹⁷	tension, const. V , eq. (2)	dicumyl peroxide
0.18	30	Shen et al. ²⁰	tension, const. P , eq. (3)	dicumyl peroxide
0.18	25-70	Barrie et al. ⁴⁷	tension, const. P , eq. (3)	unknown
0.18	50	Smith et al. ³⁶	tension, const. P , eq. (3)	γ -radiation using ⁶⁰ Co

^a P = Pressure; V = volume.

an increase in f_e/f as the strain becomes smaller, while others^{16,26,34,37} have found no significant change. In one case, a decrease has been reported.³⁸ The deviation from the constancy of f_e/f with strain maybe attributed to the term $-\beta_v T/(\alpha^3 - 1)$ in eq. (3), which was used by most of authors in calculating f_e/f .⁴⁹ The presence of the term $-\beta_v T/(\alpha^3 - 1)$ in eq. (3) implies a sensitivity to the absolute values of the strain and hence to the precision with which the unstrained length can be determined. This precision is rather poor. The $(\alpha^3 - 1)$ term is absent due to the derivation of the corresponding eq. (4), thus avoiding the problem of measurement of low strain. Table II lists the published data for f_e/f ; in cases where the figures varied with the strain, the values quoted refer to the region of higher strain, where variations were generally very small. It is found from Table II that the present results for f_e/f in compression are similar to results from previous works in tension and torsion. For example, compare

the results at 20°C from the present work with the results of Boyce et al.⁴⁹ at 20°C in torsion, in which $f_e/f = 0.126$ (see Table II).

A comparison of f_e/f from this work with that from Shen et al.¹² in tension is also particularly meaningful, because both groups used the same crosslinking agent for the samples and the same equation in calculating f_e/f . The value of f_e/f at 30°C from this work was 0.106, which is somewhat smaller than 0.15 by Shen et al.¹² This difference may be due to the different methods used in sample preparation.

In conclusion, the values of f_e/f obtained by tension and compression appear to be in reasonable agreement, at least within the limits of the sample curing procedures used. The TMA method for f_e/f is rapid and convenient, and the use of very small sample is a marked advantage.

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