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Determination of Young's Modulus of Elastomers by Use of A Thermomechanical Analyzer

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Synopsis

This work used a conventional thermomechanical analyzer (TMA) to measure the depth of indentation at room temperature of elastomers and Finkin's equation to calculate Young's moduli of elastomers, which have been measured by Drutowski, from the radius of contact of an indentor on thin sheets of sample. Data obtained from the TMA are compared with those measured by radius of contact and Hertz contact theory and are found in good agreement. Measurements of Young's modulus as a function of temperature at different heating rates by TMA were made for an acrylic elastomer. The results are compared with theory and the deviations from theory are discussed.

INTRODUCTION

Young's moduli of polymeric materials can be measured by a number of methods: Nielsen[1] in 1962 listed a table for calculation of Young's modulus from the deformations of beams. Young's modulus can also be determined from shear and bulk moduli by shear and torsional analysis[1-3] and compressibility testing.[4] Vibrating methods have been used by Joshi[5] and Buchdahl[6] to measure Young's modulus at low temperatures. Pezzin and Zinelli[7] followed ASTM D638 to determine Young's modulus of poly(vinyl chloride) (PVC) by use of an Instron tensile tester. Young's moduli of PVC fractions were obtained from the initial slopes of stress–strain curves. Moduli of natural rubbers crosslinked by dicumyl peroxide were studied by Wood et al.[8,9] as a function of time, temperature, and fraction of crosslinking agent in the compressive mode following ASTM D1415-56T, which is a commonly used way of evaluating elastomer elasticity.

The equation derived by Hertz[10,11] was used to calculate Young's modulus from the indentation of a rigid ball indentor on sample sheets. Drutowski[12] measured Young's moduli of elastomers by optical measurement of contact radius between a transparent spherical indentor and the sample based on Hertzian contact analysis. A critical comparison of this method was made with conventional hardness tests. Waters[13] has found a universal function in terms of the radio of thickness of sample to the actual radius of contact to calculate Young's moduli for thin sheets of rubber. This function is independent of ball size, applied force, and Young's modulus of the rubber. A mathematical expression was derived by Jopling and Pitts[14] for the measurement of the elastic moduli of swollen gelatin from the indentation on thin films by a flat-ended plunger. Finkin[15] recently developed an expression for Young's moduli in terms of the depth of indentation or contact radius from Vorovich and Ustinov's solution[16] for the indentation of rubber sheet by a spherical indentor. The expressions were verified by use of the published and unpublished data of Drutowski and Waters.

EXPERIMENTAL

Samples used for this experiment were essentially the same type of elastomers used by Drutowski[12] and were supplied by International Packing Corp., Bristol, New Hampshire. The sample size was approximately 15 × 15 × 0.2 cm. Measurements were made using a du Pont 900 differential thermal analyzer combined with a du Pont 941 thermomechanical analyzer.[17] Figure 1 shows a systematic description of the thermomechanical analyzer (TMA). The probe used for the TMA was a quartz rod, radius = 0.123 cm, with a hemispherical end. Samples 0.5 × 0.5 cm were cut from the sheets and placed under the end of the probe. The probe was adjusted to just touch the surface of the sample using the probe position controller. A load of constant weight was applied to the probe, and the displacement of the probe was recorded as a function of time at

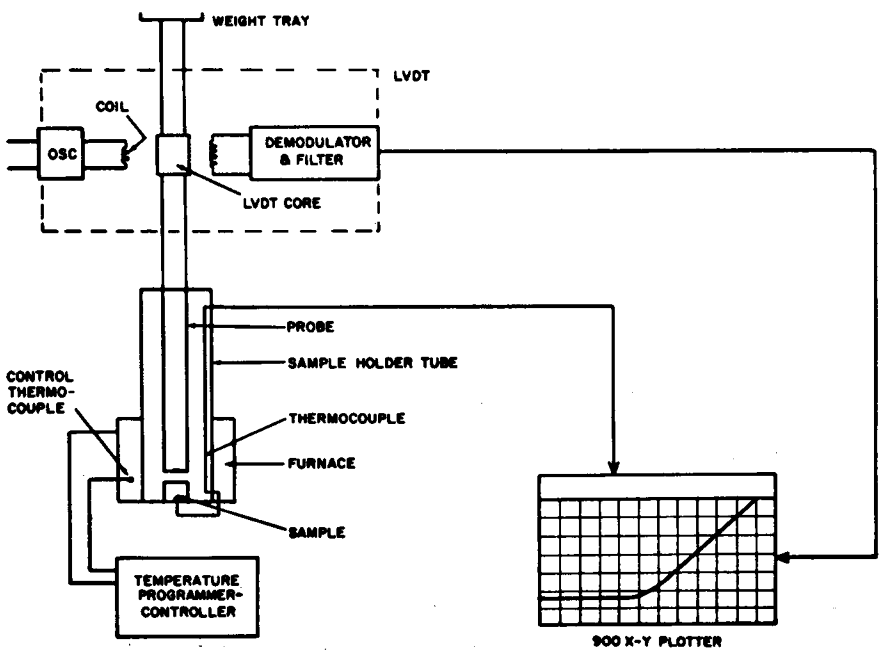

Fig. 1. Systematic description of the thermomechanical analyzer.

room temperature. For comparison with other results, various loads were tested.

RESULTS AND PRECISION

Table I shows Young's moduli of acrylic and silicone elastomers with the per cent standard deviation and the precision of measurement at each load. Young's modulus at each load was calculated from the depth of indentation at 2 min after placing the load using Finkin's equation:[15]

$$E = \frac{3PR(1-\gamma^2)}{4H^3}\left[\left(\frac{Rd}{H^2}\right)^{1/2} + 0.252\left(\frac{Rd}{H^2}\right) + 0.1588\left(\frac{Rd}{H^2}\right)^{3/2} + 0.2245\left(\frac{Rd}{H^2}\right)^2 + 0.3069\left(\frac{Rd}{H^2}\right)^{5/2} + 0.2980\left(\frac{Rd}{H^2}\right)\right]^{-3} \quad (1)$$

where E is Young's modulus, P is normal load, R is the radius of the spherically tipped indentor, H is the sheet thickness, d is the depth of indentor penetration, and γ is Poisson's ratio of the elastic layer (which for rubber is approximately equal to 0.5). Indentations on four positions of each sample were made to calculate the precision of measurement at each load as shown in column 4 of Table I. The lower precision at lower load is likely due to the manual error of the adjustment of zero displacement at no load on the probe and the buckling between sample and the base of sample holder. Young's moduli of acrylic and silicone elastomers in columns 2 and 3 at different loads were obtained from the indentation of different samples cut from four positions of the 6 in. × 6 in. sheets. The higher standard deviations at lower loads are again due to the manual error of measurement. Table II gives the comparison of Young's modulus measured from the depth of indentation with TMA from this work, E_T, from contact radius[12,15] E_R and from Hertz contact theory[11,15] E_H for acrylic and silicone elastomers. The results are in good agreement. The values of E_T measured at loads of 50 and 100 g are very close to Drutowski's nominal experimental values, which are given at the top of the table. The deviations of the values of E_T at lower loads from the nominal experimental ones are likely due to the measurement error cited previously.

TABLE I
Young's Modulus Measured by TMA

	Young's modulus E, lb/in.^{2}		
Load P, g	Acrylic elastomer	Silicone elastomer	Precision, %
100	547 ± 4.09%	1591 ± 3.6%	1.29
50	533 ± 5.05%	1514 ± 2.34%	3.94
20	480 ± 5.3%	1408 ± 4.28%	7.89
10	433 ± 8.2%	1329 ± 10.5%	13.2
5	447 ± 8.1%	1253 ± 7.02%	21.4
2	383 ± 11.7%	1099 ± 8.43%	35.7

TABLE II
Comparison of Young's Modulus E(lb/in.^{2}) Measured from the Depth of Penetration with TMA (E_T), from Contact Radius (E_R),[a] and from Hertz Contact Theory (E_H)[b] for Acrylic and Silicone Elastomers

	Acrylic elastomer (E = 510)[c]			Silicone elastomer (E = 1600)[c]		
Load, g	E_T	E_R	E_H	E_T	E_R	E_H
2	383	—	—	1099	—	—
5	447	—	—	1253	—	—
10	443	436	442	1329	1526	1521
20	480	489	499	1408	1642	1653
50	533	515	538	1514	1623	1654
100	547	550	590	1591	1560	1610

[a] From refs. 12 and 15.
[b] From refs. 11 and 15.
[c] Drutowski's (ref. 12) nominal experimental values of E.

Higher loads were not tested because the measurement would be off the scale of the instrument and the implicit limitation of eq. (1) that the radius of contact should not be greater than the thickness of the sample.[15,16] It can be concluded that for a fixed thickness and hardness of sample and a specified range of measurement, there will be an optimum applied load to obtain the most accurate value of Young's modulus by the indentation method. For this work the value appears to be 50–100 g.

Young's moduli of the elastomers were measured with relaxation method by an Instron tensile tester, and the values of E for the two elastomers were found to be about 1.7 times the nominal values. The deviations may be due to the error in measuring the cross-sectional area of the sample and the inaccuracy of the method. Young's moduli have also been measured from the indentation of a flat-ended indentor using the equation derived by Jopling and Pitts.[14] The values of E calculated were about 1.6 times the nominal value of acrylic elastomer and 1.3 times of nominal value of silicone elastomer under a 50-g load. The values of E measured with a 100-g load were much higher than the nominal values, as the indentation is less than twice that of the indentation with 50 g. The equation derived by Jopling and Pitts[14] requires that the indentation should be proportional to the applied load for the same value of Young's modulus of an elastomer. The deviations may be due to the fact that the equation derived by Jopling and Pitts is for very thin films (0.0127 cm to 0.0317 cm), so that it is inapplicable to our case. Lebedev and Ufliand[20] have developed a solution to express the displacement using a flat-ended indentor in terms of load, Young's modulus, radius of the indentor, and the thickness of sample which is close to our case. Young's modulus can be obtained from the numerical solution of a Fredholm integral equation with a continuous symmetrical kernal. The explicit expression of Young's modulus as a function of load, thickness of sample, and radius of indentor is, however, not available.

MEASUREMENTS AS A FUNCTION OF TEMPERATURE

Young's modulus can be measured as a function of temperature quickly and conveniently by TMA. The indentation as a function of temperature was measured either stepwise or by continuous temperature programming at various heating rates. For stepwise measurements, the indentation of the sample was measured first at room temperature after applying a load of 100 g overnight. The temperature of the sample was then raised and the indentation was recorded when no detectable change in indentation with time was observed, usually 1 hr. This procedure was repeated for several higher temperatures; and the indentations, after correcting for thermal expansion, were then used to calculate Young's modulus with eq. (1).

Note that the measurement of Young's modulus as a function of temperature is more conveniently made at an equilibrium state rather than at a specified time. Equation (1) was derived for equilibrium conditions.[16] In the programmed temperature case, the indentation was made at room temperature overnight as in the first case. The indentations were then recorded as a function of temperature at a selected heating rate. A sample of the same size with no load on it was run as a function of temperature at the same heating rate to determine the thermal expansion coefficient. By use of varying heating rates, Young's moduli can be determined conveniently as a function of temperature.

RESULTS AND DISCUSSION

To make a significant comparison of Young's modulus as a function of temperature at different heating rates, the ratio of measured Young's modulus to that at a selected reference temperature was used. Figure 2 shows ratios of Young's modulus as a function of temperature using a reference temperature of 25°C at various heating rates. Figures 3 and 4 show the same type of plot as Figure 2 using a slightly different experimental procedure. For results given in Figure 3, the sample was placed under a load of 100 g at room temperature overnight and then cooled to 0°, followed by temperature programming at various heating rates. Figure 4 shows results obtained by the same procedure, except that the sample was initially cooled to −125°C.

Kinetic theory[1,21] for rubber predicts that the Young's modulus of ideal rubber, E, as a function of temperature T will be given by

$$E = \frac{3\rho RT}{M_c}(1 - 2M_c/\bar{M}_n) \qquad (2)$$

where ρ is the density of the rubber, R is the gas constant, M_c is the molecular weight between crosslinking, and $\bar{M}_n$ is the number-average molecular weight of the rubber. The proportionality, providing the density and M_c are constant with temperature, of Young's modulus E versus temperature T has been confirmed by Wood[8,9,18] for natural rubber crosslinked by

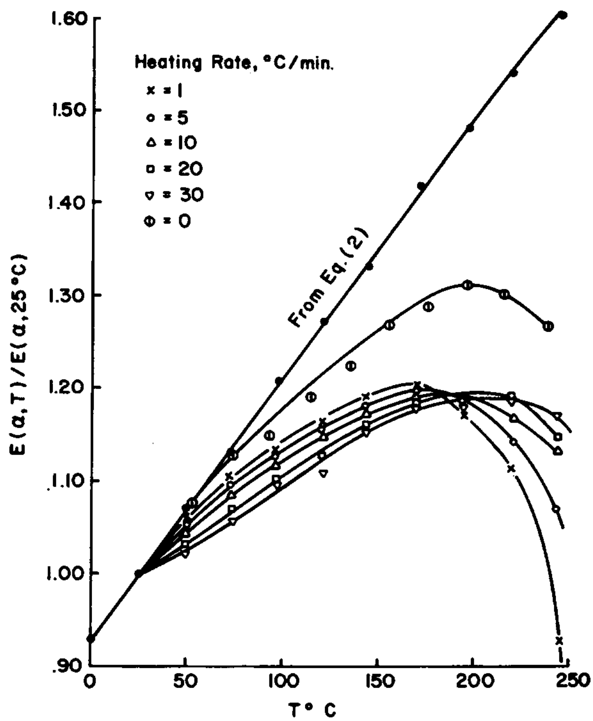

Fig. 2. Plot of Young's modulus vs. temperature with starting temperature of 25°C.

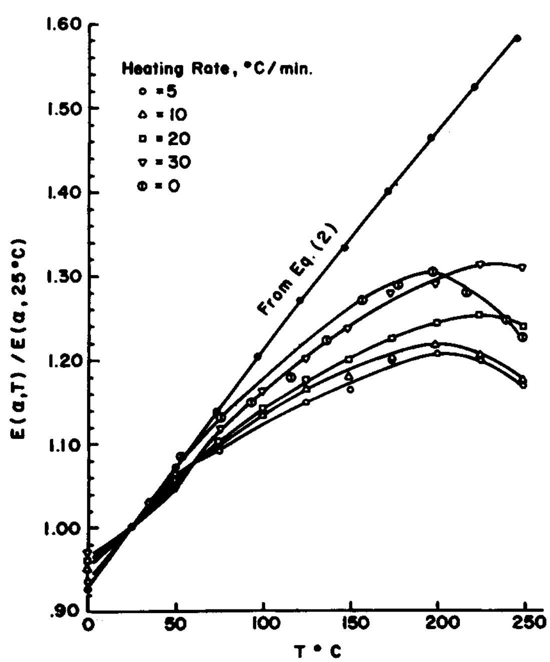

Fig. 3. Plot of Young's modulus vs. temperature with starting temperature of 0°C.

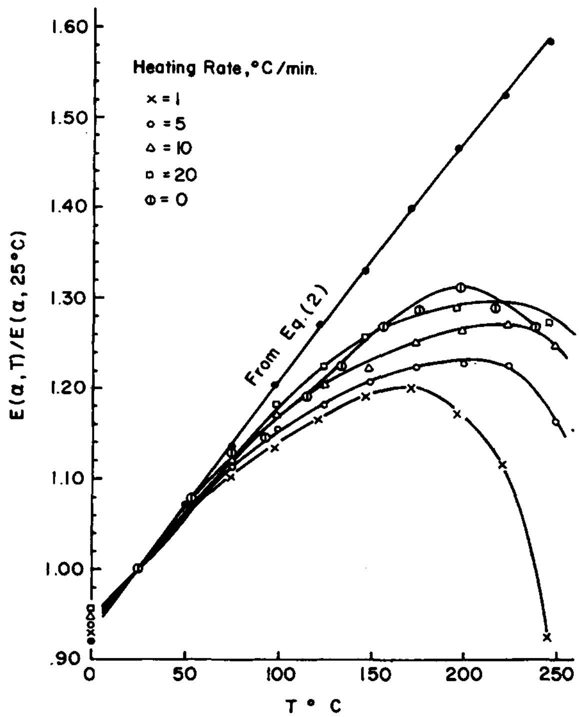

Fig. 4. Plot of Young's modulus vs. temperature with starting temperature of −125°C.

dicumyl peroxide and by Vervloet[19] for crosslinked elastomers. Plots of E versus T calculated from eq. (2) with 25°C as the reference temperature are shown on Figures 2, 3, and 4, respectively. The density has been calculated from the thermal expansion coefficient, $1.504 \times 10^{-4} {}^{\circ}C^{-1}$, for the acrylic elastomer used in this work, and M_c was assumed to be constant. From the three figures, it appears that the results with a zero heating rate, i.e., temperature increasing stepwise, follow eq. (2) very well up to 75°C. The deviation from eq. (2) at higher temperatures may be due to the amine curing agent in the elastomer dissociating from the network structure. Thus, the network structure is destroyed and the molecular weight between crosslinkage, M_c, is not constant. As shown in the figures, the greater deviations of Young's modulus at continuous heating rates is due to lack of time for the molecular chains to relax to the equilibrium state. The maximum point of the curves is the temperature at which the retractive force is compensated by the softening of the sample. This temperature increases with heating rate, possibly owing to the longer time for relaxation at lower heating rates.

The higher deviations from eq. (2) at higher heating rate in the low-temperature region are due to lack of time to achieve the equilibrium state. The ratios change appreciably when the starting temperature is changed. The temperature range at which the deviation from eq. (2) is observed at higher heating rates is higher than that of lower ones as the starting temperature is lowered, as shown in Figures 3 and 4, starting at 0°C and −125°C, respectively. Note that the plot of Figure 4 starts at 0°C because eq. (1) is inapplicable for calculating Young's modulus at temperature lower than the glass transition temperature (−10°C for the elastomer used).

The use of TMA to measure Young's modulus of elastomers as a function of temperature and time is a rapid and convenient method and has a major advantage in that only a small amount of sample is needed. The degree of crosslinking of the elastomers can also be determined according to eq. (2) provided Young's modulus is known by other means. The accuracy of using a TMA to determine Young's modulus could be improved if the output of the current thermal analyzer could be amplified further or by use of a digital readout recorder to read the small change in indentation as the temperature is changing. It may also be desirable to use a flat-ended plunger instead of the hemispherical-ended one as the equation which relates Young's modulus to indentation variables is available. The slip of the plunger as temperature is raised is more easily eliminated with a flat-ended indentor.

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