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The thermoelastic effect in PMMA

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The thermoelastic effect has been measured in polymethylmethacrylate under both tensile and compressive uniaxial stress and the resulting temperature change for a known applied stress has been used to calculate the linear expansion coefficient of PMMA over a range of temperatures from 295 to 355 K and uniaxial stress in the elastic range using the Thompson relationship:

$$\Delta\theta = -\alpha T\Delta\sigma/\rho C_p \, .$$

Results are shown to agree with other measurements on the same material. An unexplained variation of α with stress has been observed at low values of applied stress. Values of the simple Grüneisen coefficient (γ_G) have been calculated over the same ranges of temperature and stress from the relationship:

$$\gamma_G = 3\Delta\theta\, B_s/T\Delta\sigma \, .$$

1. Introduction

The thermoelastic effect in solids was predicted by Thompson [1] and demonstrated in iron and rubber by Joule [2]. The derivation of Thompson's equation describing the change in temperature of a solid under uniaxial stress in its elastic range may be found in textbooks. A particularly useful exposition is given by Benton [3].

The usual form of the relationship is:

$$d\theta = -\alpha T\, d\sigma/\rho\, C_p \, ,$$

where $d\theta$ = change in temperature for an increase in uniaxial tensile stress $d\sigma$,
α = linear expansion coefficient at temperature T K,
ρ = Density of the solid at T K and applied uniaxial tensile stress,
C_p = specific heat of the solid at constant pressure and T K. (C_p may also be a function of stress.)

Later Grüneisen [4, 5] obtained the relationship

$$\lambda = 3\alpha = \gamma_G\, C_V\rho/B_T = \gamma_G\, C_p\rho/B_S$$

where λ = volume expansion coefficient of solid,
γ_G = Grüneisen constant,
C_V = specific heat at constant volume,
ρ = density of solid,
B_T = isothermal bulk modulus,
C_p = specific heat at constant pressure,
B_S = adiabatic bulk modulus.

The Grüneisen constant, γ_G, has been shown to be substantially invariant over wide temperature ranges for a number of metals [4].

The validity of Thompson's equation has been demonstrated for metals by a number of workers [2, 5-7]. Wagner [8] showed that in the case of silver iodide, which has a negative coefficient of expansion, the sign of the temperature change is reversed as theory predicts. Much work has also been done on the effect in rubber [9], in which the sign of the temperature change is also reversed. Very little has been done to measure the effect in plastics where large values of thermal expansion coefficient suggest that a larger temperature change might be observed for a given applied stress and where low thermal conductivity of the solid might be expected to facilitate the measurement of small temperature changes by reducing losses to the environment. Some measurements were made on films of cellulose nitrate and cellulose acetate by McNally and Sheppard [10] in which the thermoelastic effect was observed. The values of $d\theta$ which they obtained do not, however, fit simple theory. More recently qualitative results have been reported by Binder and Muller [11].

2. Experimental method

2.1. Compression

Discs of polymethylmethacrylate 17.4 mm in diameter and 0.25 in. (6.35 mm) in thickness were prepared in specially designed moulds which allowed the incorporation of two thermocouples near the centre of the disc. The effect of sample dimensions was not studied. In order to reduce the thermal mass of the thermocouples to a minimum and also to reduce heat transport by conduction along the leads, the thinnest available chromel and alumel wire (25 μm diameter) was used. Junctions were made by spot welding. Mouldings were carried out by cutting two PMMA discs of the required diameter from 0.125 in. (3.175 mm) thick Perspex sheet (I.C.I.). The thermocouples were sandwiched between the two discs in a split mould, the leads being led through the holes provided for the purpose. The sample was then moulded in a hot press under a light pressure about $\frac{1}{2}$ t in.$^{-2}$ (approx. 8 MN m^{-2}) at a temperature of 130°C for half an hour and then rapidly cooled.

Calibration of the encapsulated thermocouples was checked by enclosing the sample in a polythene bag in a temperature-controlled water bath, the temperature recorded by the thermocouple meter (Comark 1601 or 1604) being compared with that recorded by a mercury-in-glass thermometer in the bath. The thermocouples were found to agree within 0.5°C over a range from 25°C to 100°C.

A temperature-controlled box was built to enclose a Monsanto tensometer. The box was heated by two 100 W electric light bulbs, the current to which was supplied from a proportional controller (Ether 12-98) controlled from a chromel-alumel thermocouple within the environmental chamber, the air in which was circulated by a fan.

The disc samples were placed between the compression jaws of the tensometer either in a Perspex sample holder or merely taped to one of the jaws by masking tape. No significant difference in behaviour was observed using these differing methods.

The signals from the two thermocouples (which were found to agree to within 0.2%) were added by connecting the two in series via a cold junction at 0°C. The output was taken to a thermocouple amplifier (Comark 1604) which gave a voltage output of 0 to 1 V for a selected 10°C range of temperature. The meter controls could be used to provide an off-set zero so that it was possible to select any given 10°C range from $-$ 60°C to $+$ 170°C in which to operate. The output of the amplifier was fed to a further combined amplifier and recorder (Varian Associates G15-2). The maximum sensitivity of the overall system was found to be $\pm 2 \times 10^{-3}$ °C on the most sensitive range, the limitation being electrical noise in the amplifiers and/or the thermocouple. It was found necessary to screen the sample from incident radiation (from room lighting, radiant heat sources within the environmental chamber, etc.) by a loose cover of aluminium foil.

Stress was applied using the tensometer as a hand-operated device since the motor drive was found to produce electrical noise. It was found necessary to surround the thermocouple amplifier with an expanded polystyrene case to prevent small temperature variations due to draughts causing short-term changes in the amplifier output.

Readings were taken by applying measured compressive stress to the sample and observing the resultant temperature rise on the recorder. Stress was then removed and the resulting fall in temperature observed. This procedure was repeated at least three times for each value of applied stress. The sample temperature was allowed to stabilize before each series of experiments until the trace on the recorder chart remained at a steady value. This took from 2 to 20 h, dependent on the temperature difference between the environmental chamber and room temperature. At the end of each series of measurements, the temperature of the sample was measured using the signal from the encapsulated thermocouples.

Stresses beyond about 50 MN m^{-2} were found in general to be undesirable since there was a danger that at higher stresses results would be complicated by the onset of creep. In general the maximum stress applied was approximately 42 MN m^{-2} and at higher ambient temperatures even this value proved too large and measurements were terminated at the first sign of creep, detected by a small but just measurable fall in the applied stress with time.

Measurements of the variation of specific heat with temperature were made over the range 310 to 373 K using a differential scanning calorimeter (Perkin-Elmer DSC-2).

2.2. Tension

Attempts were made to measure the thermoelastic effect on applying uniaxial stress using strip test-pieces into which thermocouples had been embedded by substantially the same method as that used to prepare test-pieces for compression experiments. These measurements were

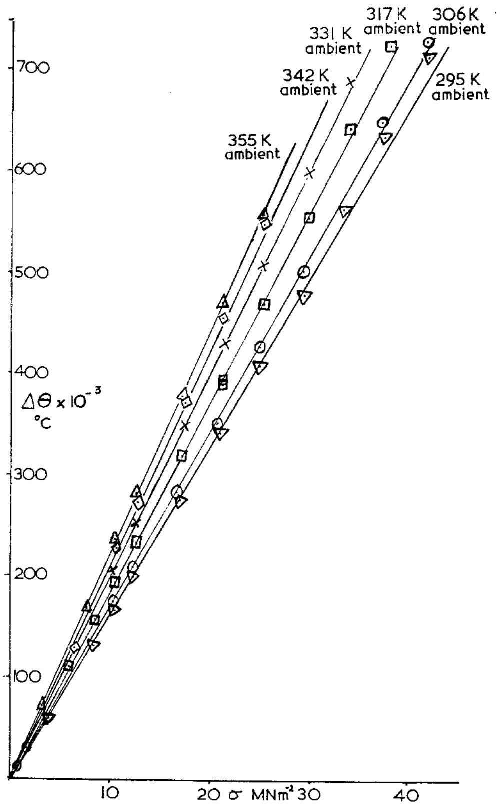


Figure 1 Change in temperature with applied uniaxial compressive stress.

unsuccessful since the encapsulated wires proved to be a source of weakness in the strips leading to fracture at quite low stress. To avoid weakening the test-piece, therefore, measurements were made using thermocouples sandwiched between two strips of 1.588 mm thick plastic, 12 mm wide and 100 mm in length between grips, the thermocouples being trapped in position during the course of the experiment. This arrangement proved moderately satisfactory though there was more thermal noise than in the case of the compression measurements due to the junctions being exposed to the air and in less-perfect thermal contact with the plastic.

Measurements were made in the same stress range as that used in the compression experiments.

3. Results

3.1. Compression

Measured values of $\Delta\theta$ at a given stress and temperature fell within ± 5% of the mean, and in most cases within ± 3% for the stress range 4 to 42 MN/m^{-2}. Below 4 MN m^{-2} the scatter was somewhat greater due to the greater difficulty in measuring the small thermocouple signals. Values shown in the figures are mean values based on at least six readings for each point.

Fig. 1 shows a plot of $\Delta\theta$ versus σ: Fig. 2 shows the same results plotted as $\Delta\theta$ versus T for a range of stress values, values of $\Delta\theta$ having been adjusted to the standard value of stress where necessary – such corrections being small in all cases.

The Grüneisen constant γ_G was calculated

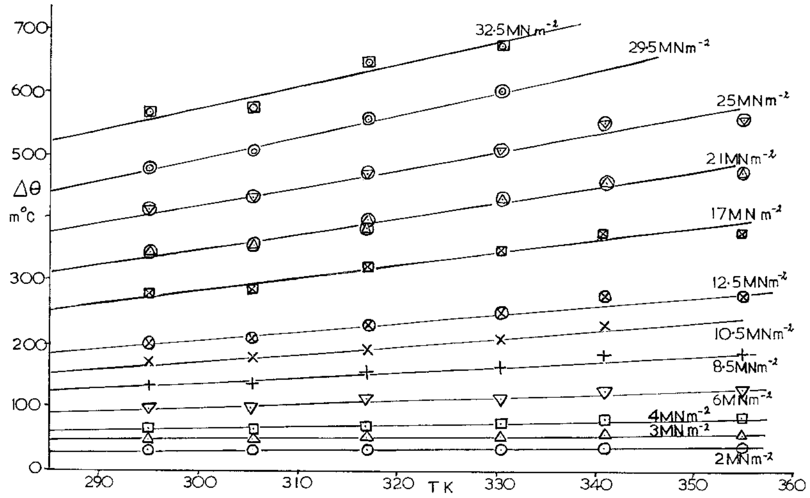


Figure 2 Change in temperature with uniaxial compressive stress against ambient temperature.

over the range of temperature and uniaxial stress from the relationship:

$$\gamma_G = 3\Delta\theta \,.\, B_S/T\sigma$$

The values of adiabatic bulk modulus, B_S, were obtained from the data of Asay *et al.* [12]. Values for ρ were obtained from [15]. No significant variation of γ_G with temperature was observed over the temperature range studied. Mean value of γ_G in the range 10 to 40 MN m^{-2} is 0.995 ± 0.014. Below 10 MN m^{-2} lower values were observed as in the case of α (Table I).

Values of linear expansion coefficient were calculated from

$$\alpha = \Delta\theta \; C_p\, \rho/T\sigma \, .$$

The values of C_p used in the calculation were measured in this laboratory using the Perkin-Elmer differential scanning calorimeter (D.S.C. 2). Comparisons of our results for PMMA with those of Wunderlich and Baur [13] and the low temperature measurements of Melia [14] are given in Fig. 3.

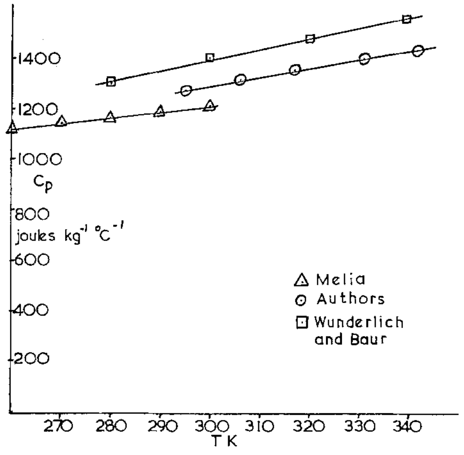


Figure 3 C_p versus T in PMMA.

3.2. Tension

Figs. 4 and 5 show the results obtained in the tensile experiments plotted as $-\Delta\theta$ versus σ and $-\Delta\theta$ versus T respectively. Values of the linear expansion coefficient were calculated in a similar way to that used for the results of compression experiments. Fig. 7b gives the values of α obtained plotted as a function of stress.

4. Discussion

4.1. The variation of density with uniaxial stress

It can be shown that the density of a solid varies with uniaxial compressive stress according to the equation:

Density under applied uniaxial stress

$$= \rho_0/(1-\sigma/E)(1+\mu\sigma/E)^2$$
$$\simeq \rho_0/\{1+(2\mu-1)\sigma/E\}\,(\sigma/E \ll 1)$$

where ρ_0 = zero stress value of ρ, μ = Poisson's ratio, E = modulus of elasticity.

4.2. Variation of specific-heat with stress

The variation of specific heat with uniaxial stress is given by [3]:

$$(\partial\alpha/\partial T)_\sigma = \rho_0(\partial C_p/\partial\sigma)_T/T \, .$$

Taking $(\partial\alpha/\partial T)_\sigma = 4 \times 10^{-7}$ °C^{-2} ($T = 300$ K) and $\rho_0 = 1.2 \times 10^3$ kg m^{-3}.

then if $(\partial C_p/\partial\sigma)_{300K} = 10^{-7}$ J kg^{-1} °C^{-1} N^{-1} m^{-2} taking $\sigma_{max} = 50$ MN m^{-2}, $\Delta C_p = 5$ J kg^{-1} °C^{-1}.

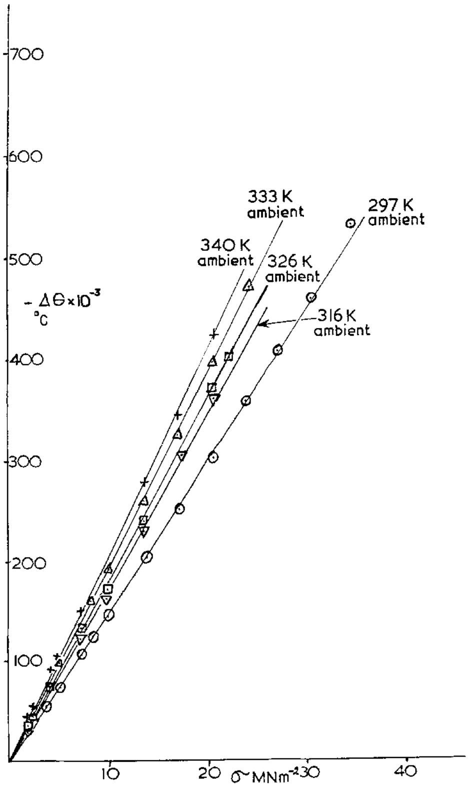


Figure 4 Change in temperature with applied uniaxial tensile stress.

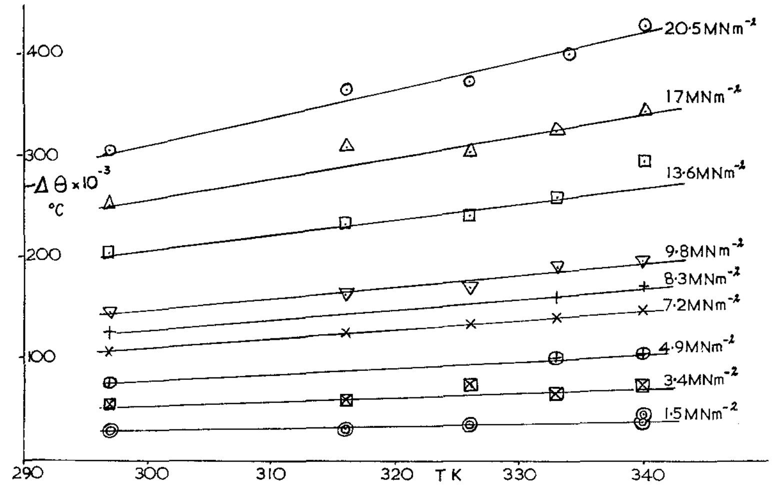


Figure 5 Change in temperature with uniaxial tensile stress against ambient temperature.

The room temperature value of $C_p \simeq 1300$ J kg^{-1} °C^{-1}; therefore, the change in C_p represents less than $\frac{1}{2}\%$ under the maximum stress used in these experiments.

4.3. Variation in adiabatic bulk modulus B_S with stress

If the increase in pressure is taken as $\frac{1}{3}$ applied uniaxial stress, then maximum pressure increase in the present experiments is 14 MN m^{-2} (0.14 kbar). From the values of Asay *et al.* [12] this represents a change in B_S at maximum stress of about 1.8 to 2.0 kbar over the temperature range of the experiments. This represents a change of approximately 3% over the stress range used.

4.4. $\Delta\theta$ as a function of stress

$\Delta\theta$ gives in general a good straight line fit as a function of stress for both compression and tensile results (Figs. 1 and 4). The results show an increase in the slopes of the lines with increasing temperature, both in the case of compressive and tensile experiments. Such an increase is to be expected from theory.

Figs. 2 and 5 show the variation of $\Delta\theta$ with temperature for a range of stress values. The

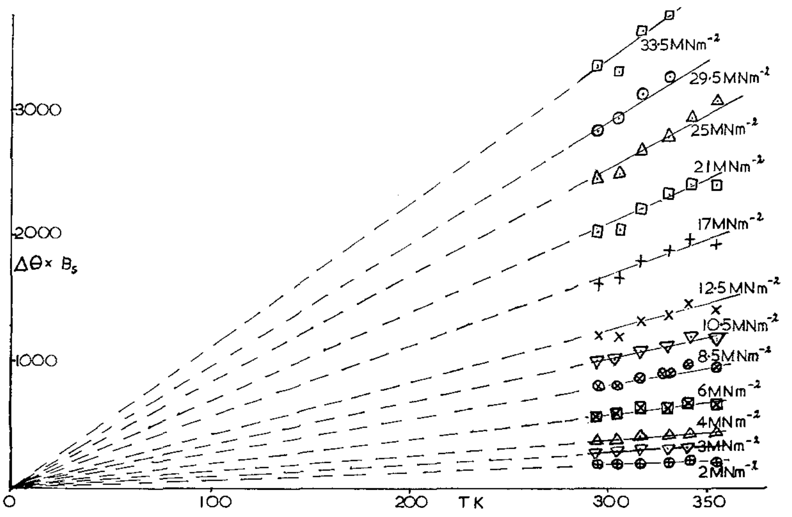
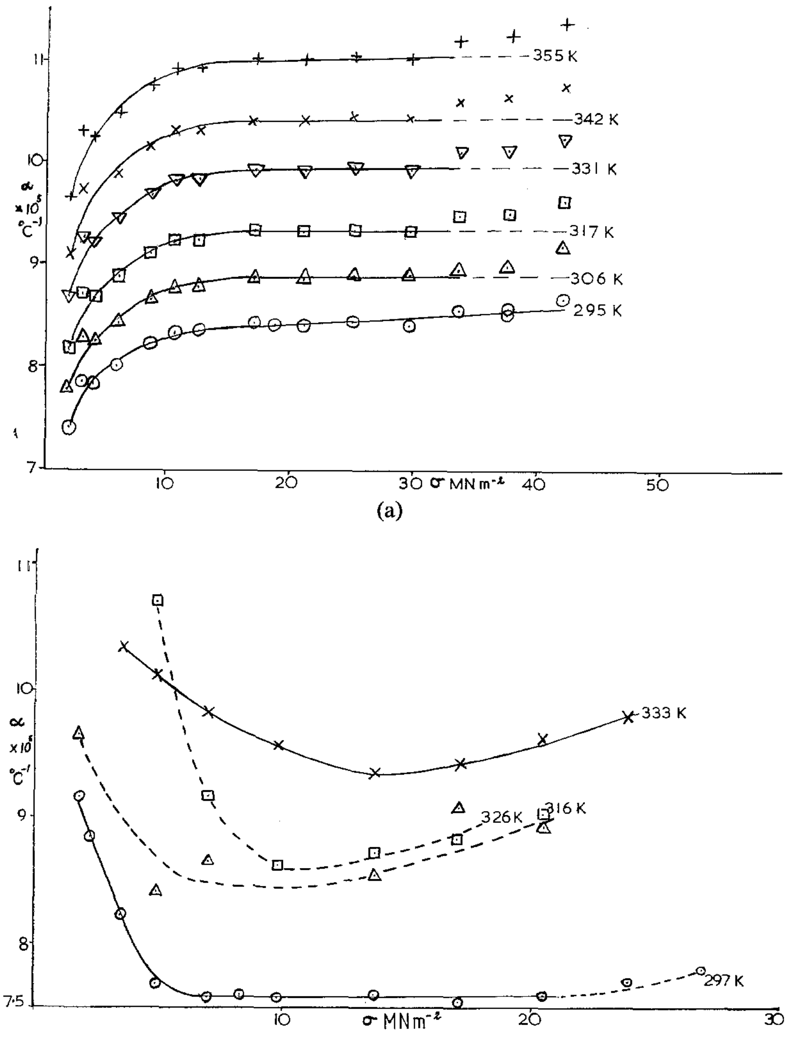


Figure 6 $\Delta\theta \times B_S$ as a function of ambient temperature (compression results).



(a)

(b)

Figure 7 (a) Estimated linear expansion coefficient plotted against uniaxial compressive stress. (b) Estimated linear expansion coefficient plotted against uniaxial tensile stress.

curves are straight lines over the limited temperature range of the experiments, but extrapolation of the best least squares fits to the points does not give intercepts at absolute zero, an observation to be expected due to the known variation of B_S with temperature. In Fig. 6, $\Delta\theta \times B_S$ is plotted against temperature for the compression results. Within the limits of experimental error the points give a reasonable fit to a family of straight lines which extrapolate to 0 K, as indicated, suggesting that the Grüneisen constant is substantially invariant with temperature over the temperature range studied. As, in other cases, the tension results gave greater scatter and in this case no conclusion could have been reached from them.

Figs. 7a and b indicate that linear expansion coefficient varies sharply with uniaxial stress at low stresses, rising in the case of compression measurements and falling in the case of tensile measurements. At higher stress the value calculated from compression results becomes almost constant, rising only slightly with stress. Results from tensile experiments are less accurate but indicate a sharper rise with increasing stress after passing through a minimum. This effect is not at present understood. It may be that the observed behaviour is due to errors involved in the measurement of the small signals encountered at low stresses, though the non-random nature of the deviations would seem to conflict with such an explanation. It is of interest in this connection that McNally and Sheppard [10] observed a similar phenomenon on measuring the linear expansion of films of cellulose nitrate under uniaxial stress using a more conventional method. Another possible explanation may lie in the absence of complete parallelism in the sample A face in compression or in chuck alignment in tension.

The calculated variation of α with temperature from compression results agrees well with the zero stress value calculated from data supplied by the manufacturers [15] and Wilson and Treloar [18] (see Table I). Values of α calculated from the lowest stress (2 MN m^{-2}) results are in excellent agreement with these data (Table I), but values obtained from the "plateau" regions of Fig. 7a are some 15% higher than these zero stress values. Values of α obtained from tensile experiments (Fig. 7b) are less certain due to the inferior accuracy of these measurements but lie between the zero stress values from [15] and the uniaxial compressive stress values in the "plateau" region.

Calculated values of the Grüneisen constant, γ_G, over the whole temperature and compressive stress range show that this parameter is substantially constant with temperature but increases with increasing uniaxial compressive stress. The only value for (PMMA) in this temperature range which we have been able to find in the literature is a single point given by Barker [16] (Fig. 1 of this reference). The exact value obtained is not given, but an estimate from the figure shows it to lie within the range of values calculated from our results.

The experiments described have been designed to avoid any effects of creep by keeping the applied stress low. It should be noted, however, that since in tension the thermoelastic effect leads to a reduction of temperature whereas energy used up in creep is generally assumed to lead to an increase in temperature, this method of study affords, in principle, a means of distinguishing between differing mechanisms of deformation.

5. Summary

The thermoelastic effect in polymethylmethacrylate has been measured over a range of temperature from 295 to 355 K and a range of uniaxial stress from 2 to 42 MN m^{-2}, measurements having been made both in compression

TABLE I Values of the linear coefficient of expansion devrived from thermoelastic measurements.

	Temperature (K)					
	295	306	317	331	342	355
ρ_0 (kg m^{-3}) [15]	1186	1183	1179	1175	1171	1167
c_p (J kg^{-1} °C^{-1})	1271	1310	1348	1392	1424	1462
B_S (MN m^{-2}) [12]	5910	5761	5612	5422	5273	5097
α (°C^{-1} × 10^5) [15]	7.38	7.82	8.26	8.82	9.26	9.78
α (°C^{-1} × 10^5) [18]	7.39	7.65	—	—	—	—
σ (MN m^{-2})	α (× 10^5°C^{-1})					
2.0	7.36	7.76	8.17	8.70	9.12	9.66
3.0	7.86	8.29	8.73	9.30	9.75	10.32
4.0	7.85	8.25	8.68	9.25	9.69	10.26
6.0	8.01	8.45	8.89	9.47	9.93	10.51
8.5	8.21	8.66	9.12	9.71	10.18	10.78
10.5	8.34	8.80	9.27	9.87	10.35	10.95
12.5	8.35	8.79	9.25	9.86	10.33	10.94
17.0	8.43	8.89	9.36	9.97	10.45	11.06
21.0	8.42	8.88	9.35	9.96	10.44	11.05
25.0	8.46	8.92	9.39	10.01	10.49	11.10
29.5	8.43	8.89	9.36	9.97	10.45	11.06
33.5	8.58	9.05	9.53	10.15	10.64	11.26
37.5	8.61	9.08	9.56	10.18	10.68	11.30
42.0	8.72	9.20	9.68	10.31	10.81	11.44

TABLE II Values of γ_G (calc) $= 3(\Delta\theta/T\sigma)\,B_S$

	Temperature (K)						
(MN$^{\sigma}$ m^{-2})	295	306	317	331	342	355	G^{mean}
2.0	0.962	0.819	0.863	0.836	0.925	0.785	0.865
3.0	0.982	0.941	0.965	0.885	0.941	0.862	0.929
4.0	0.962	0.861	0.929	0.921	0.948	0.894	0.919
6.0	0.962	0.906	0.956	0.934	0.987	0.905	0.941
8.5	0.955	0.910	0.987	0.965	1.023	0.948	0.965
10.5	0.979	0.947	0.976	0.983	1.018	—	0.980
12.5	0.976	0.940	0.994	0.991	1.025	0.948	0.979
17.0	0.984	0.950	1.007	1.010	1.028	0.959	0.989
21.0	0.990	0.952	1.002	1.010	1.008	0.971	0.989
25.0	0.990	0.969	1.003	1.004	1.025	0.963	0.992
29.5	0.977	0.967	1.004	1.004	—	—	0.988
33.5	1.015	0.966	1.026	1.017	—	—	1.005
37.5	—	0.985	1.033	—	—	—	1.009
42.0	1.045	0.987	1.030	—	—	—	1.021

and tension. Values of linear expansion coefficient have been calculated from the results and are in reasonable agreement with values obtained by more conventional methods. Values obtained from the more reliable compression results were as follows: α (295 K) 8.4×10^{-5} K^{-1} and for the Grüneisen constant 0.99. An unexplained variation in linear expansion coefficient with stress has been observed in both uniaxial tension and compression at low stress values where the experimental error is greatest. The thermoelastic effect affords a method of determining α and γ_G as functions of both temperature and uniaxial stress within the elastic range.

Appendix. Stress concentration at the thermocouple junction

On application of uniaxial compressive stress to the sample, one would expect a higher value of stress in the region of the thermocouple junction and leads than in the bulk material. Such an increase in stress at the detecting element might be expected to lead to error in the observed signal, since the temperature of the junction and the plastic in its immediate neighbourhood would initially be higher than that of the bulk of the sample. A rigorous analysis of the decay of a heat pulse so produced is a complicated problem in three-dimensional heat flows, involving the conduction of heat away from the junction into the bulk of the plastic and also heat flow down the thermocouple leads. The thin thermocouple wire used in the experiments has a very small thermal capacity and the sensing element will react rapidly to changes in the temperature of its immediate environment. As a first approximation to the heat flow problem we can take a highly simplified model in which the region around the junction is taken as a solid bounded by two planes at $x = 0$ and l, maintained at temperature $\theta = \theta_i$ whilst the solid is initially at some uniform temperature $\theta_i = 0$ (representing the heat pulse due to stress concentration). Then θ_i is the temperature difference between the junction and the bulk of the plastic. The solution to the heat flow problem is [17]:

$$\theta(x, t) = (4\theta_i/\pi) \sum_{n=0}^{\infty} \{1/(2n + 1)\} \exp\{-K(2n + 1)^2\pi^2 t/l^2\} \,.\, \sin\{(2n + 1)\pi x/l\}\,.$$

We are only concerned with the temperature at $x = l/2$ (representing the thermocouple junction) which gives:

$$\theta(l/2, t) = (4\theta_i/\pi) \sum_{n=0}^{\infty} \{(-1)^n/(2n + 1)\} \exp[-K(2n + 1)^2\pi^2 t/l^2]\,.$$

Assuming that maximum stress (at the thermocouple) is three times the applied stress in the bulk polymer, then change in temperature at the junction would be three times that in the bulk at $t = 0$. Assume also that stress concentration around the thermocouple extends three times the wire diameter on each side of the wire. Then we can write $\theta_i = 2\Delta\theta$ and $l = 150$ µm if the wire diameter is 25 µm. $\Delta\theta$ = temperature rise in bulk of polymer.

Taking $K = 1.2 \times 10^{-6}$ m^2 sec^{-1} calculation shows that $\theta(l/2)$ falls to within 0.1% of the temperature in the bulk in approximately 0.15 sec, which is short compared with the duration of a measurement.

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