

Thermal Effects in Polytetrafluoroethylene at High Hydrostatic Pressures

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Synopsis

The temperature changes as a result of rapid hydrostatic pressure applications are reported for polytetrafluoroethylene (PTFE, Teflon) in the reference temperature range from 294° to 381°K and in the pressure range from 13.8 to 200 MN/m². The thermal effects were found to be higher at the reference temperature approximating the transition temperatures of 19° and 30°C than at higher reference temperature. The data were analyzed by determining the predicted thermoelastic coefficients derived from the Thomson equation ($\partial T/\partial P = \alpha T/\rho C_p$). A curve-fitting analysis showed that the empirical curve, $(\partial T/\partial P) = ab(\Delta P)^{b-1}$, described the experimental thermoelastic coefficients obtained from the experiments. The fact that no agreement was found between the predicted and the experimental coefficients is due to the physical changes in PTFE at the transition temperatures. The relationship between the thermal effects and the chain molecular motion is discussed by including dynamic mechanical analysis and differential scanning calorimetry DSC measurements for the PTFE samples.

INTRODUCTION

It is well recognized that the rapid deformation of a solid usually results in a temperature change in the material. This rapid deformation is closely related to an adiabatic process whereby the heat absorbed or generated during the deformation, changes the temperature of the material. For many years, these thermal effects have been assumed to be relatively small because the pioneering work in metals showed that, in fact, that was the case.¹⁻⁷ However, for polymeric materials, recent studies have shown that these thermal effects are relatively large.⁸⁻¹²

Two classic examples can be found in rubber and steel. For instance, a rubber band warms up when it is stretched and cools down when it is released, whereas the opposite is found for steel.

These thermal effects, also termed the *thermoelastic effect*, were predicted by Thomson^{1,2} and demonstrated in iron and rubber by Joule.^{3,4} The derivation of the Thomson equation describing the magnitude of the temperature change as a result of a small change in pressure under adiabatic conditions can be found elsewhere.^{1,2,13} The classical Thomson equation can be written as:

$$\frac{\partial T}{\partial P} = \frac{\alpha T_0}{\rho C_p}$$

where α is the volume thermal expansion coefficient, C_p is the specific heat, ρ is the density, and T_0 the reference temperature. The term $(\partial T/\partial P)$ is

usually defined as the thermoelastic coefficient. For small pressures, the term $\alpha T_0/\rho C_p$ is assumed to be independent of pressure and temperature. Upon integration of the Thomson equation within reasonable limits, the temperature changes ΔT as the result of rapid pressure applications ΔP , can be estimated. This procedure may be valid for small pressure applications but it would be severely limited in its usefulness in predicting temperature changes resulting from large pressure changes. This is because the parameters α , ρ , and C_p are much more pressure sensitive for polymers than for either metal or ceramics. Many of the thermoelastic studies have been conducted under uniaxial tension or uniaxial compression.¹⁴⁻¹⁶ Recently we have shown that the use of hydrostatic pressures to determine the thermal effects in polymers have the advantage of minimizing shear effects, a concern commonly found in the measurements of the thermoelastic effect under tensile or compressive deformation.¹⁷

Data on the thermoelastic effect in polymers is very limited. No report has been issued on the thermoelastic effect in polytetrafluoroethylene (Teflon, DuPont trademark). The solid-state transitions at 19° and 30°C reported for PTFE made this material unique in determining the thermal effects.¹⁸ This will give us insight into what might be the effect of chain flexibility or molecular transitions on the thermal effects.

EXPERIMENTAL

The sample of PTFE used in this work was obtained from Cadillac Plastics and Chemical, Co. as Teflon rod of 1/4 inches (6.35 mm) outside diameter (OD). Most probably, rods were made by ram extrusion using initially free-flowing powders or presintered resins obtained from DuPont Company.¹⁸ The standard specific gravity (SSG) of the Teflon rod was $2.265 \times 10^3 \text{ kg/m}^3$. The specific gravity was determined after completion of the thermoelastic measurements indicating that the rod may have gone through a densification process as the result of the high hydrostatic pressure applications. This explains the unusually high specific gravity (average 2.14 to 2.19). Although the degree of crystallinity was not directly measured, it is well accepted that Teflon extruded rod shows a typical crystallinity range of 55-68%.¹⁹

The apparatus and evaluation procedure for obtaining the temperature changes resulting from the rapid applications of pressure were described previously.¹⁷ The samples (0.635 cm OD and 9.22 cm long) was contained in the center of the high pressure cell. Liquid mercury was used to transmit the pressure to the sample. Hydrostatic pressures were achieved by using a 1-hp air compressor and an air-driven high pressure reciprocating pump. The pressure was measured with two Bourdon gauges, each with a maximum of 50,000 psi and sensitivity of 500 psi/division. The temperature changes were recorded using two iron-constantan thermocouples. The measuring junction was located in the geometric center of the rod sample, whereas the reference junction was located outside the high pressure unit. This arrangement allowed us to measure directly only the temperature differences generated by the pressure variations and with maximum sensitivity since, when

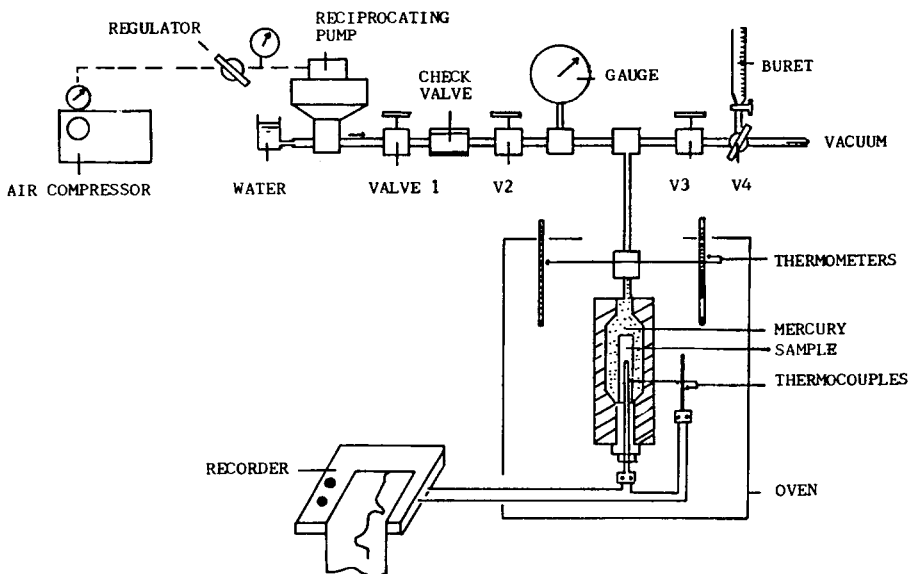


Fig. 1. The high pressure system.

both junctions were at atmospheric pressure, the output of the thermocouple was virtually zero. Figure 1 illustrates schematically the experimental setup.

Pressure was rapidly applied by opening a valve which caused the selected pressure to be transmitted almost instantaneously to the sample (a "pressure jet"). An increase in temperature was recorded. The pressure was released by the rapid opening of a second valve to atmospheric pressure which resulted in a decrease in temperature in the polymer sample. Figure 2 shows a typical recording of the thermal effects. In the figure, we observe the following steps.

- From (A) to (B) represents the initial state where P_0 is the atmospheric pressure and T_0 is the reference temperature or temperature of the oven.
- At (B) a pressure is applied, P_{on} .
- From (B) to (C) an increase in temperature $\Delta T_{(+)}$ in the sample is recorded.
- From (C) to (D) the sample relaxes until it reaches approximately the initial temperature T_0 .
- At (E) the pressure is rapidly released.
- From (E) to (F) a decrease in temperature $\Delta T_{(-)}$ in the sample is measured.
- From (F) to (G) the sample returns to the initial conditions P_0 and T_0 .

The dynamic mechanical analysis was determined by using a mechanical spectrometer, Rheometrics, Inc., RMS-605 model, with torsional cylindrical fixtures.

A differential scanning calorimeter (DSC), Model DuPont 1090, was used to determine the thermal analysis of the Teflon rod. The heat capacity data was kindly determined by Dr. Robert Haker of DuPont Company.

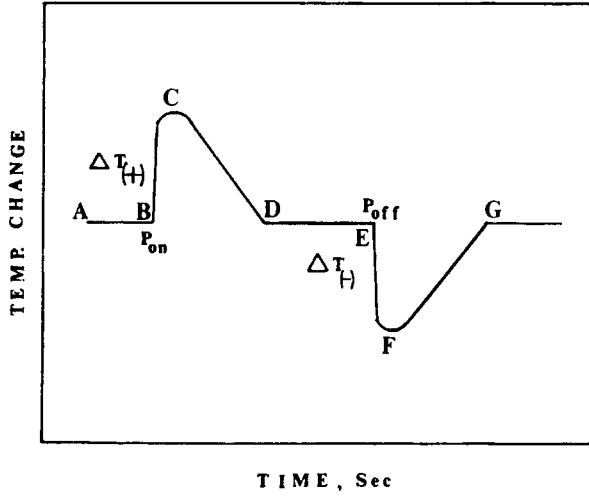


Fig. 2. Representation of the reversible thermal effects.

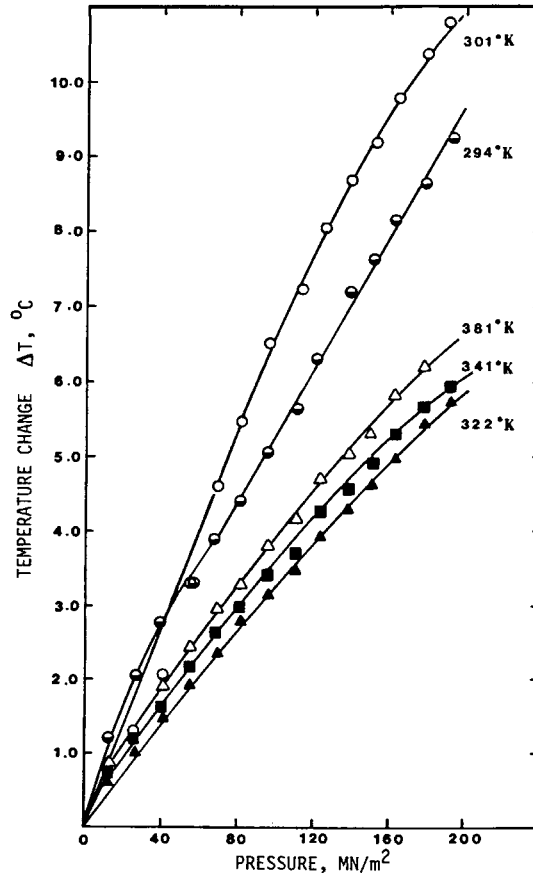


Fig. 3. Temperature changes as a function of applied pressure for PTFE at different reference temperatures.

RESULTS AND DISCUSSION

Figure 3 presents some of the temperature changes as a function of the applied pressure at different temperatures. The thermal effects for the reference temperatures of 294° and 301°K were partially reversible. That is, the increase in temperature upon rapid application of pressure $\Delta T_{(+)}$ was larger than the decrease in temperature $\Delta T_{(-)}$ for the release of pressure. An approximate 25% difference between $\Delta T_{(+)}$ and $\Delta T_{(-)}$ was observed for this case.

For the reference temperature range from 322° to 381°K, the thermal effects were found to be fully reversible. That is, $\Delta T_{(+)} = \Delta T_{(-)}$.

The temperature changes plotted in Figure 3 correspond to the rise in temperature for the reference temperature of 294° and 301°K, whereas those for the reference temperatures from 322° to 381°K correspond to the average between the increase and decrease in temperature change.

Two interesting effects were found. First, the temperature changes at the reference temperatures of 294° and 301°K were found to be larger than those measured for the reference temperatures from 322° to 381°K. Second, for the range 322–381°K, the temperature changes increased as the reference temperature increased. To illustrate this, at $\Delta P = 137.9 \text{ MN/m}^2$ the temperature changes $\Delta T = 7.2^\circ$ and 8.7°C were measured at 294° and 301°K, respectively.

However, for the same pressure applied, the temperature changes of $\Delta T = 4.3^\circ$, 4.51° , and 5.03°C were recorded for the reference temperatures of 322°, 341°, and 381°K, respectively.

Figure 4 shows the dependence of the temperature changes on the reference temperatures at selected pressures. When plotted in this way, the temperature changes reached a maximum near the T_g , decreased and then increased steadily with the reference temperature.

To evaluate the experimental data in terms of the Thomson equation, the values for the specific gravity, the heat capacity, and the thermal expansion coefficient were taken from different sources and are shown in Table I. The specific volume dependence on pressure and temperature for PTFE was reported by C. E. Weir^{20,21} and selected values were taken for the calculations.²² The heat capacity data measured for our PTFE rods were in complete agreement with the specific heat data reported by Marx and Dole²³ for PTFE.

TABLE I
Physical Data for Polytetrafluoroethylene

Temperature (°K)	Specific gravity (kg/m ³)	Specific heat (J/kg°C)	Volumetric thermal expansion (1/°K)	Thermoelastic ^a coefficient $\partial T/\partial P$ (°C/MN m ⁻²)
294	2.2173×10^3	1.416×10^3	2.595×10^{-4}	2.430×10^{-2}
301	2.2126×10^3	1.372×10^3	2.595×10^{-4}	2.573×10^{-2}
322	2.1987×10^3	1.066×10^3	3.039×10^{-4}	4.217×10^{-2}
341	2.1873×10^3	1.061×10^3	3.039×10^{-4}	4.465×10^{-2}
381	2.1600×10^3	1.082×10^3	3.039×10^{-4}	4.954×10^{-2}

^a Predicted from $\partial T/\partial P = \alpha T_0/\rho C_p$.

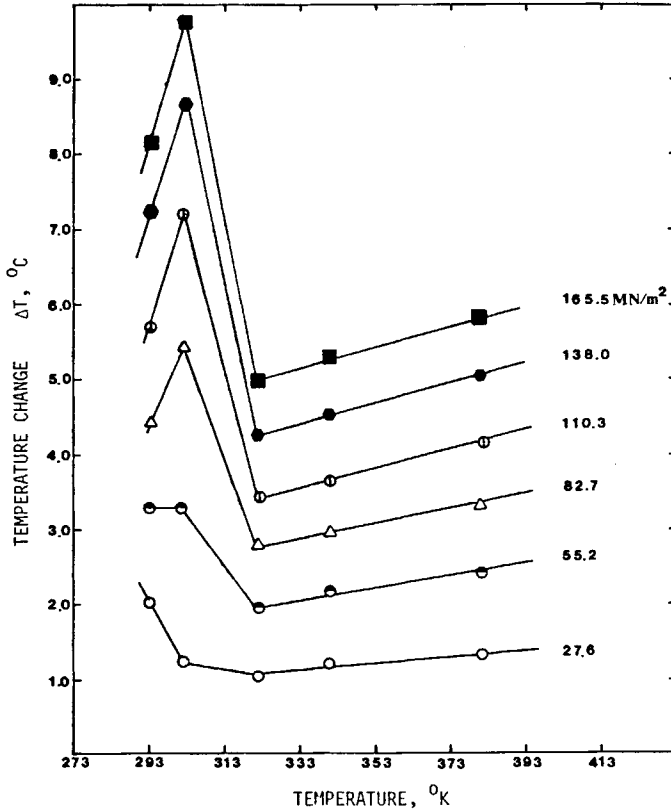


Fig. 4. Temperature changes as a function of the reference temperature for PTFE at selected applied pressures.

The volumetric coefficient of thermal expansion was taken from volume-temperature relationships for the room temperature transition in PTFE.³⁶ Thus, the thermoelastic coefficient ($\partial T/\partial P$) predicted from the Thomson equation could be estimated. They are also shown in Table I.

A curve-fitting analysis was done to determine the experimental thermoelastic coefficients from our data. It showed that the best and simplest curve fit was obtained from the empirical equation $\Delta T = a(\Delta P)^b$.

Table II shows the results of the curve-fitting analysis. If $\Delta T = T - T_0$ and $\Delta P = P - P_0$, where T_0 is the reference temperature and $P_0 = 1_{\text{atm}}$, and differentiating on both sides of the above empirical equation, we obtain

$$dT = ab\Delta P^{(b-1)}dP$$

Then, the experimental thermoelastic coefficients can be approximated to

$$\frac{\partial T}{\partial P} = ab(\Delta P)^{b-1}$$

This equation shows a clear dependence of the thermoelastic coefficients on

TABLE II

Values for a and b in the Empirical Equation $\Delta T = a(\Delta P)^b$ Obtained from the Curve-Fitting Analysis for PTFE

Temperature (°K)	a	b	Coefficient of determination R^2
294	0.1585	0.7664	1.00
301	0.0417	1.0797	0.99
322	0.0579	0.8730	1.00
341	0.0703	0.8458	1.00
381	0.1091	0.7759	0.99

the pressure supplied. This equation is purely empirical and no effort was given to correlate it with thermodynamic variables. Table III shows the thermoelastic coefficients determined from selected pressures.

The Thomson equation predicted a linear temperature or the reference temperature. It was not able to predict the unexpected thermal effect at 294°K and 301°K, relatively larger than for higher reference temperatures. Thus, large differences were found between the experimental and the predicted thermoelastic coefficients for PTFE as can be seen in Tables II and III.

The dynamic mechanical analysis was done for two samples at 1 Hz frequency of forced vibration. One sample was used as received and the second was annealed in an oven at 170°C for 24 hours. Two runs were done on each sample by quenching them with liquid nitrogen. The temperature sweep was from -130°C to 230°C. The shear storage modulus G' , the shear loss modulus G'' , and the dissipation factor, $\tan \delta$, were determined from these measurements. They are plotted as a function of temperature in Figure 5.

TABLE III

Experimental Thermoelastic Coefficients ($\partial T/\partial P$) Determined for PTFE at Selected Pressures

Temperature (°K)	$\frac{\partial T}{\partial p} = ab(\Delta P)^{b-1}$	ΔP (MN m ⁻²)	$\frac{\partial T}{\partial P}$ (°C/MN·m ⁻²)
294	$0.1215 \times (\Delta P)^{-0.2336}$	0.1013	0.2074
		20	0.0603
		100	0.0414
301	$4.5013 \times 10^{-2}(\Delta P)^{0.07971}$	0.1013	0.0375
		20	0.0572
		100	0.0650
322	$5.0547 \times 10^{-2}(\Delta P)^{-0.1270}$	0.1013	0.0676
		20	0.0346
		100	0.0282
341	$5.9460 \times 10^{-2}(\Delta P)^{-0.1542}$	0.1013	0.0846
		20	0.0375
		100	0.0292
381	$8.4632 \times 10^{-2}(\Delta P)^{-0.22413}$	0.1013	0.1414
		20	0.0432
		100	0.0302

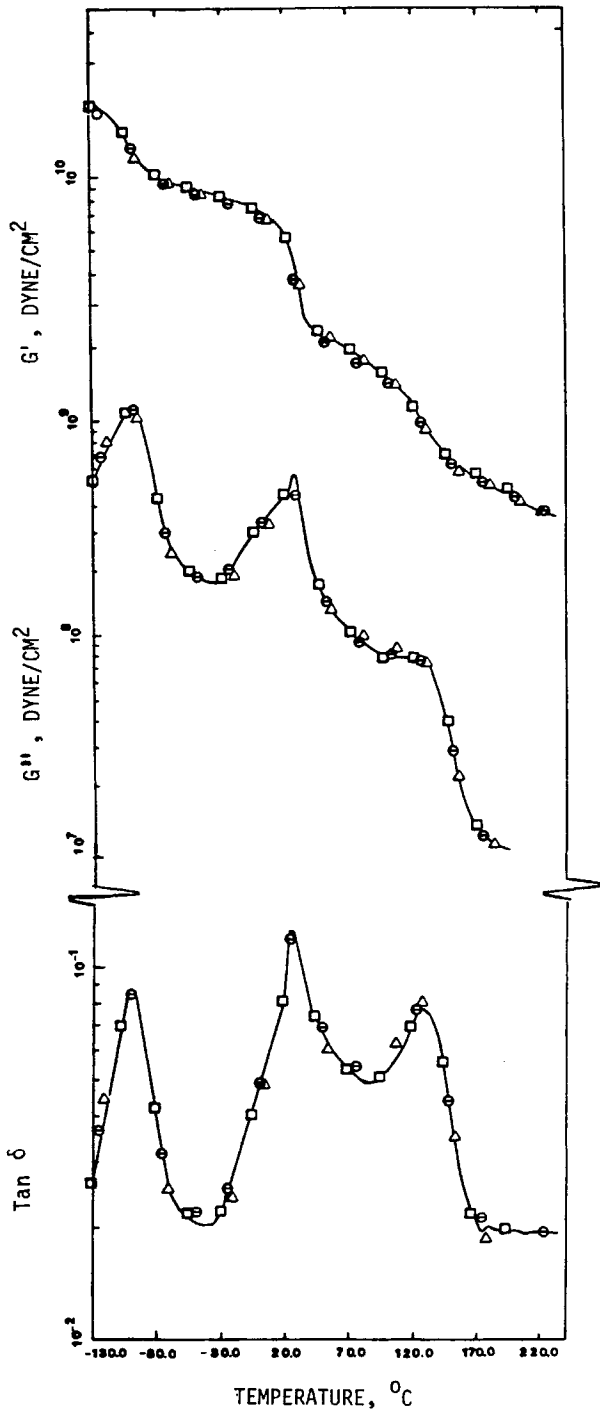


Fig. 5. G' , G'' , and $\tan \delta$ values for PTFE as a function of temperature at 1 Hz and 0.1% deformation.

No differences were found between the annealed PTFE sample and the one used as received. Our DMA results agree with the internal friction study of PTFE reported by McCrum.²⁴ In the temperature range from -130°C to 230°C , four relaxation regions were measured at -99°C (174°K), 22°C (295°K), 30°C (303°K), and 130°C (403°K) as determined from the $\tan \delta$ values.

Extensive work has been reported on transitions for PTFE.^{18,25-28} Effects of structural changes on properties such as specific heat, specific volume, dynamic mechanical and electrical properties are observed at these transitions. Apart from the transition at the melting point, the transitions at 19°C and 30°C are perhaps of greatest consequence because they occur around ambient temperature and significantly affect the product behavior.

The second-order transition at -99°C is usually assigned to the amorphous region describing the onset of rotational motion around the C—C bond.²⁴ The first-order transition at 19°C corresponds to the crystalline region describing the angular displacement causing disorder. Above 19°C , the triclinic pattern changes to a hexagonal unit cell. Around 19°C , a slight untwisting of the molecule from a 180° rotation per 13 CF_2 groups to a 180° twist per 15 CF_2 group occurs. At the first-order transition at 30°C the hexagonal unit cell disappears and the rodlike hexagonal packing of the chains in the lateral direction is retained. Below 19°C there is almost perfect three-dimensional order, at 19 – 30°C , the chain segments are disordered, and above 30°C the preferred crystallographic direction is lost and the molecular segments oscillate above their long axes with a random regular orientation in the lattice.

The melting point measured for the PTFE rod was 326.1°C at 5 deg/min in an air flow of 30 ml/min. The DSC scan is shown in Figure 6. The melting point reported for the remelted PTFE is 327°C .²⁷

The DSC scan for the temperature range 0 – 50°C was repeated three times by cooling it rapidly with liquid nitrogen. In Figure 7 the scan B corresponds to the sample run after melting. It shows well defined transition at 20.4°C

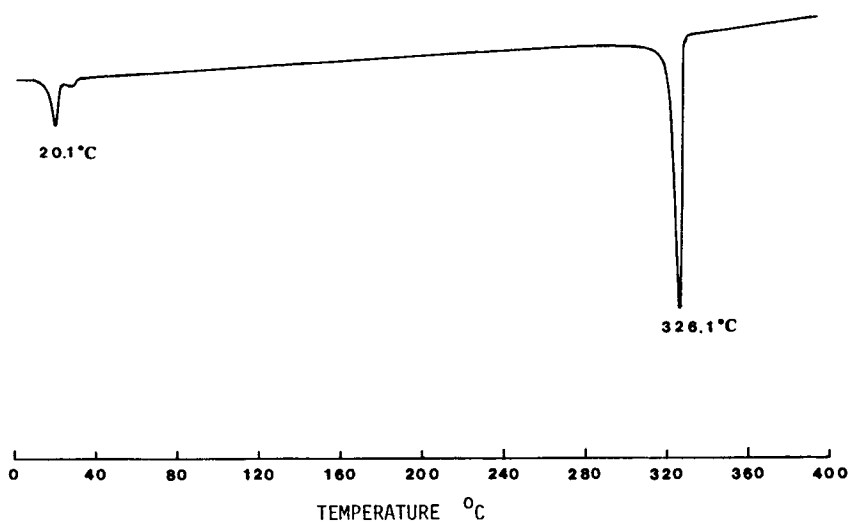


Fig. 6. DSC scan for PTFE at 5 deg/min in air flow at 30 ml/min.

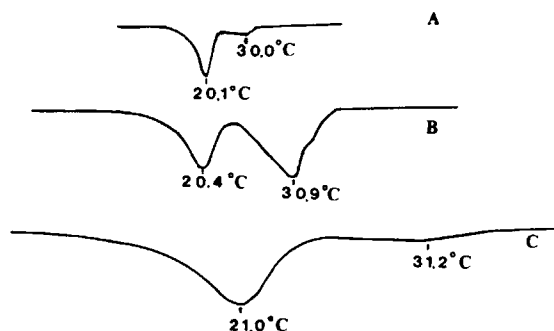


Fig. 7. DSC scans for PTFE in the temperature range from 10° to 40°C.

and 30.9°C. Scans A and B show transition at 20.1–21°C and a weak but measurable transition at 30–31°C.

The dissipation factor, $\tan \delta$, is a measure of the ratio of energy dissipated as heat to the maximum energy stored in the material during one cycle deformation. In addition, the shear loss modulus, G'' , is directly proportional to the heat H dissipated per cycle as given by:

$$H = \pi G'' \gamma_0^2$$

where γ_0 is the maximum value of the shear strain during a cycle.²⁸ Thus, when a viscoelastic material such as PTFE is submitted to a deformation near its first or secondary transition, relatively large energy losses or heat dissipation effects can be measured. In fact, this is probably what is happening with the thermal effects measured at the reference temperatures of 294° and 301°K. These two reference temperatures are close to the transitions at 19°C and 30°C observed for PTFE. Consequently, the rapid application of pressure resulted in higher thermal effects at reference temperatures near the transition temperature of the sample.

As discussed above, the thermoelastic coefficient ($\partial T/\partial P$) defined the thermal effects associated with rapid pressure changes. This thermoelastic coefficient differs from the transition temperature dependence on pressure described in the Clapeyron equation

$$\frac{dP}{dT_g} = \frac{\Delta H}{T\Delta V} = \frac{\Delta S}{\Delta V}$$

where ΔH is the enthalpy, T is the absolute temperature, ΔV is the volume change, ΔS is the entropy, and P is the pressure of the phase transition. The subscript symbol g is written to differentiate between the thermoelastic coefficient and the Clapeyron coefficient (dP/dT_g). The Clapeyron equation has been found to apply in any change or state or phase transformation. For example, the dependence of the melting point on pressure for PTFE has been used to determine the latent heat of fusion.²⁹ The heat of transition was also determined for PTFE at the transition temperatures of 20°C, 30°C, and 130°C by means of the Clapeyron equation.^{30,31}

From our thermoelastic data at 294°K and 301°K, the coefficient dT_g/dP could be estimated by assuming that $dT_g/dP \cong \partial T/\partial P$ at the room temperature transitions. From Table III and for $\Delta P = 0.1013 \text{ MN/m}^2$ (1 atm), the coefficients $\partial T/\partial P$ are 0.20743 and 0.0375 °C/MN m^{-2} for the reference temperatures of 294°K and 301°K.

The temperature increase of the transition at 19°C with pressure of about 0.013°C/atm (0.128°C/MN⁻²) has been reported.^{32,33} The pressure dependence of the room temperature transition for PTFE could also be estimated from the equation $(dT_g/dP) = \Delta\beta/\Delta\alpha$,³⁴ where $\Delta\beta = \beta_2 - \beta_1$ the compressibility above (β_2) and below (β_1) the transition and $\Delta\alpha = \alpha_2 - \alpha_1$, the thermal expansion coefficient. C. Weir³⁵ reported the compressibility for PTFE from this $\Delta\beta = \beta_2 - \beta_1 = 1.05595 \times 10^{-5} - 6.474 \times 10^{-6} = 4.086 \times 10^6 \text{ 1/atm}$.

F. A. Quinn et al.³⁶ estimated the thermal expansion coefficients. Thus, $\Delta\alpha = \alpha_2 - \alpha_1 = 3039 \times 10^{-4} - 2.595 \times 10^{-4} = 4.4400 \times 10^{-5} \text{ 1/}^\circ\text{C}$. Then, $dT_g/dP = 0.90835 \text{ }^\circ\text{C/MN}^2$ for the room temperature transition of 20°C for PTFE.

Yasuda and Araki³⁰ determined the (dT_g/dP) coefficients for various polytetrafluoroethylenes in room temperature transition at atmospheric pressure. The values (dT_g/dP) varied in the range from 0.1517 to 0.2077 °C/MN⁻². The last value in this range agrees with the coefficient $(\partial T/\partial P)$ at 21°C determined from our thermoelastic measurements. From the Martin and Eby results,³¹ the (dT_g/dP) estimated was approximately 0.1733 °C/MN⁻².

All these values are comparatively shown in Table IV. The differences in dT_g/dP found may arise from differences in the degree of crystallinity of the samples and in the nonequilibrium character of these transitions.

The initial state of the PTFE is a very critical issue in these calculations. For instance, virgin or unmelted PTFE powder shows shifted transitions (17°, 20°, and 28°C) when compared with the remelted PTFE samples (19° and 30°C). All these transitions were reported to be subjected to superheating and are a function of the cooling rate.²⁷

The nonequilibrium nature of the room temperature transitions was also confirmed in our DSC data. Scan B in Figure 7 shows a more intense peak

TABLE IV
 dT_g/dP Values Determined for PTFE at the 20°C Transition

Our data approximating $\frac{\partial T}{\partial P} \cong \frac{dT_g}{dP}$	$\frac{\partial T}{\partial P} = 0.2074 \text{ }^\circ\text{C/MN m}^{-2}$; at $\Delta P = 0.1013 \text{ MN m}^2$ (Table III)
Beecroft and Swenson ^{32,33}	$\frac{dT_g}{dP} = 0.128 \text{ }^\circ\text{C/MN m}^{-2}$
From the equation $\frac{dT_g}{dP} = \frac{\Delta\beta}{\Delta\alpha}$ ³⁴	$\frac{dT_g}{dP} = 0.908 \text{ }^\circ\text{C/MN m}^{-2}$
Yasuda and Araki ³⁰	$\frac{dT_g}{dP} = 0.1517 - 0.2077 \text{ }^\circ\text{C/MN m}^{-2}$
Martin and Eby ³¹	$\frac{dT_g}{dP} = 0.1733 \text{ }^\circ\text{C/MN m}^{-2}$

at 30.9°C than scan A. Following cooling and reheating the character of these transitions changed as seen in scan C. The time effects in these transitions were also noticed in our thermoelastic measurements, where the temperature changes at room temperature fluctuated within a range, for each pressure applied. Measurements were carried out several times to obtain the most reproducible values. All these facts will affect the dT_g/dP values and may explain the differences found between them.

It is perhaps convenient to mention that the pressure dependence of T_g as determined using different equations and for different polymers showed a similar degree of scattered data as observed for PTFE.³⁴

Finally, changes in the entropy of the room temperature transition corrected to constant volume have been estimated to be about 0.0067 cal/deg g.³³ Martin and Eby³¹ calculated the enthalpy and entropy changes of 1.815 cal/g and 0.00621 cal/g °K, respectively after correcting for the effects of volume changes. They also showed that the enthalpy and entropy of transition increased with pressure. Therefore, it is possible that for the room temperature transition of PTFE, the changes in the chain conformation, the free volume, and the intermolecular distances between chains are closely related to these changes in entropy and enthalpy. Thus, the thermal effects measured may be associated to the entropy and enthalpy changes occurring during very rapid deformation near the room temperature transitions.

To conclude, the thermoelastic effect in PTFE is intrinsically related to the transition temperatures observed at 19° and 30° C. Higher temperature changes were measured near these transitions indicating that molecular motions in the material are associated with the higher thermal effects.

Special thanks to Dr. Robert S. Hanker of the DuPont Company for measuring the specific heat data for the Teflon rod and who also provided much of the available literature on the properties of PTFE.

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