

Thermal Expansion of Polytetrafluoroethylene (Teflon) From -190° to $+300^{\circ}$ C

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The linear thermal expansion of four samples of Teflon was determined. The results for annealed Teflon are indicated in a plot of the expansion versus temperature and in a table listing the average coefficients of linear expansion from -190° to $+300^{\circ}$ C. The effect of internal residual stresses on the expansion of Teflon was studied and found to be considerable. The first-order transitions at 20° and 30° C are clearly shown in a plot of the coefficients of expansion versus temperature.

1. Introduction

Polytetrafluoroethylene (Teflon), $[-CF_2-CF_2-]_n$, is a thermoplastic resin that is made by polymerizing tetrafluoroethylene, $CF_2=CF_2$, at high temperatures and pressures [1].¹ The carbon and fluorine atoms in the long molecules of Teflon are arranged in the form of a helix, a full 360° twist every 26 carbon atoms along its length [2].

Above 330° C, Teflon is transparent and is in a state similar to that of a liquid, in that it is free of strain and has no crystalline structure [1, 3]. At about 325° C, Teflon starts to crystallize on cooling and becomes opaque and waxy in appearance [3]. X-ray diffraction patterns indicate that the orientation is parallel with the axes of the molecules (two-dimensional) and that the crystallization continues until the temperature is slightly above room temperature [2]. At about 30° C a first-order transition occurs [4, 5], which is probably due to small and unequal longitudinal displacements of the molecules [2]. At about 20° C a much larger first-order transition occurs [4, 5, 6], which is probably due to a rotation of the molecules around their axes [2]. The expansion due to the transitions at 20° and 30° C is reversible on heating and cooling if the temperature is slowly changed. A slight hysteresis will occur during rapid heating, and a large hysteresis will occur during rapid cooling [4]. At temperatures below 15° C, X-ray diffraction patterns indicate a three-dimensional orientation [2].

Because the long polymer molecules are not straight over their entire length, the structure of Teflon is never completely crystalline. Instead, only small regions of the structure are crystalline where straight sections of a group of molecules come together in parallel alignment. These small crystalline regions are scattered throughout the material and are tied together in a random fashion by the long molecules that pass through two or more of them [1].

Teflon has a very outstanding chemical stability [1, 3]. At room temperature it is not affected by any of the usual inorganic acids or by organic solvents and is attacked only by the alkali metals and fluorine or fluorine-forming compounds at high temperatures and pressures. Teflon is also an outstanding elec-

trical insulator for high-voltage or ultra-high-frequency applications [7]. Because of its very low coefficient of friction very few substances will stick to it, and it can be used as an oil-free bearing. Teflon has one of the highest thermal stabilities of any known polymer, maintaining many of its useful properties up to 300° C. It volatilizes at a very slow rate below 400° [8], but, because of the toxicity of the gases evolved, sustained temperatures of over 200° C should not be used without proper ventilation.

Although several investigations of the thermal expansion of Teflon have been made, only two of them have been published [4, 9]. These publications were mainly concerned with the abnormal behavior of Teflon around 20° and 30° C and only reported single values for the coefficients of expansion immediately below and above these temperatures. The purpose of this investigation is to report reliable values of the linear thermal expansion of Teflon over as wide a range of temperature as practical for this material. The results are given in two figures and a table.

2. Samples and Experimental Procedure

Four samples of Teflon were investigated, as indicated in table 1. The coefficients of linear thermal expansion that are reported for these samples were determined after the samples had been annealed by heating to about 350° C and cooling slowly. The values for the density of the samples listed in table 1 were also determined after annealing. The variations between the densities are probably due to differences in forming techniques (pressure, temperature, and length of time of the molding or extruding process) [9].

TABLE 1. Description of Teflon samples investigated

Sample ^a	Method of forming	Length	Diameter	Density at 25° C (annealed)
A	Extruded-----	mm 76	mm 12.7	g/cm ³ 2.162
B	do-----	118	9.5	
C	do-----	300	19.0	2.180
D	Molded-----	119	19.0	2.12

^a Samples A, B, C, and D have laboratory numbers 1867, 1871, 1868, and 1853, respectively.

¹ Figures in brackets indicate the literature references at the end of this paper.

A time-temperature curve was obtained on sample A on both heating and cooling and a single transition was located at about 323°C . This temperature is in accord with previous investigations [1,3].

The fused-quartz tube and dial-indicator method [10] was used for the linear expansion tests on samples A, B, and D. The dial indicator was graduated to 0.0001 inch. The weight of the fused-quartz rod and the spring in the dial indicator produced a force of about 150 grams on each sample in the direction of its axis.

The linear expansion of sample C was determined with the precision micrometric method [10]. In this apparatus the sample is in a horizontal position with no external forces applied in the direction of its axis.

The cubical expansion of a sample (100 mm long) cut from the same rod as sample C was determined² with a hydrostatic weighing method [11].

The temperatures of the samples were measured with a thermocouple placed in a hole near the center of each sample, except in the cubical expansion test where a thermometer was used to measure the temperature of the water near the sample. Temperatures below room temperature were obtained by using ice, dry ice, and liquid air as the refrigerants. Most of the observations of expansion were taken when the temperature of the sample was constant.

² This determination was made by Lt. J. E. Overberger, USA, Walter Reed Army Medical Center, guest worker in Organic and Fibrous Materials Division of the National Bureau of Standards.

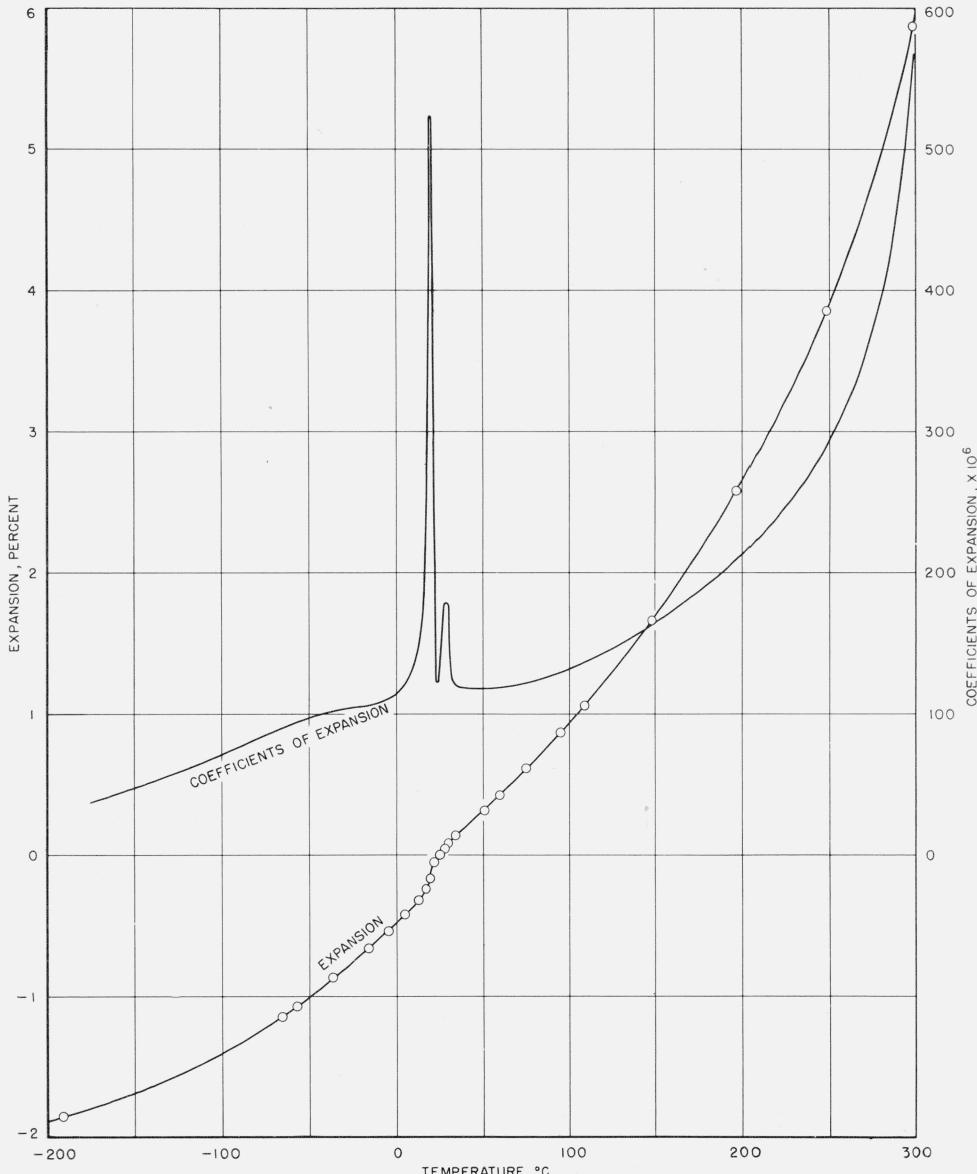


FIGURE 1. Linear thermal expansion and coefficients of linear thermal expansion of annealed Teflon (sample A).

3. Results and Discussion

In the course of this investigation not only were most of the observations of expansion made on sample A but they were also made over a much wider temperature range than on the other samples. Figure 1 shows the curve for the linear expansion of sample A from about -190° to $+300^{\circ}$ C in the annealed condition and the curve for its corresponding coefficients of expansion. The points to which the expansion curve was fitted, as indicated in the figure, are averages of the actual observations and are plotted as the expansion from an arbitrary zero at 25° C. This temperature was chosen because it is located about midway between the transitions at 20° and 30° C.

The curve representing the coefficients of expansion versus temperature was obtained by calculating the average coefficients between the actual consecutive observations of expansion and correcting them so that they represent the true thermodynamic coefficients of linear thermal expansion $\alpha = (1/L) (dL/dt)$, where L is the length at t° C. This curve shows quite clearly the first-order transitions at 20° and 30° C and also indicates the great increase in the rate of expansion at temperatures approaching the transition at 323° C.

The results of the expansion measurements on all four samples from 0° to 110° C in the annealed condition are shown in figure 2. The curve represents the expansion of sample A and is the same as

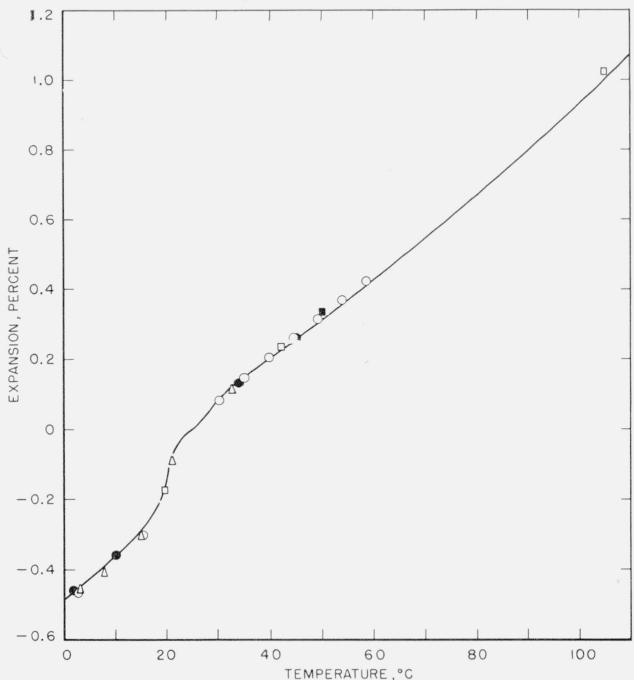


FIGURE 2. Comparison of the linear thermal expansions of four samples of annealed Teflon.

Every expansion test is plotted as zero at 25° C. The curve represents the expansion of sample A; O, first test of sample B; ●, second test of sample B; □, linear expansion test of sample C; ■, cubical expansion test of sample C plotted as linear expansion; Δ, test of sample D.

in figure 1. Figure 2 indicates that the expansions of all four samples are comparable. In fact, their expansions can be shown to be equal within the experimental error found in the measurements of expansion of sample A alone.

It was found during the course of this investigation that the length and thermal expansion of Teflon are greatly affected by residual stresses within the samples. This was demonstrated by comparing the expansion and/or length of each sample in the annealed condition with their corresponding properties in a strained condition.

After sample D had been annealed it was machined from a 0.75-inch diameter to a 0.58-inch-diameter rod. This treatment apparently had the effect of stretching the sample because after a second annealing it was found to be shorter by 1.9 percent. The effect of this induced strain was to decrease the rate of expansion by about 14 percent.

Samples A and C were found to be 7.4 and 4.9 percent longer, respectively, in the annealed condition than they were in their extruded conditions.

Before sample B had been annealed its expansion was determined from 0° to 35° C and was found to be 20.9 percent lower than it was after it had been annealed. Correspondingly its length was found to be 7.2 percent longer. After it had been annealed and the expansion determined, the sample was heated to about 300° C with an axial pressure sufficient to cause it to be permanently shortened by 1.2 percent. Its expansion was again determined from 0° to 35° C and was found to be 9.2 percent larger. After a second annealing the length and expansion of the sample were found to be approximately what they had been after the first annealing.

The change in length of Teflon due to the transitions at 20° and 30° C is about 0.24 percent. This value was obtained by constructing the tangents to the expansion curve immediately below and above these transitions and determining the difference between them at 20° C. This value is not in good agreement with the values of Rigby and Bunn [9] and Quinn, Roberts, and Work [4]. The former reported a change in volume of about 1 percent (0.3 percent in length) due only to the transition at 20° C, and the latter reported a change in volume of 1.23 percent (0.41 percent in length) due to both transitions. The above differences could be explained if their samples were more crystalline than the ones used in this investigation. A partial explanation can be based on the effect of residual stresses in their samples as they apparently were not annealed.

Table 2 gives the average coefficients of linear thermal expansion of Teflon in the annealed condition between 25° C and various other temperatures from -190° to $+300^{\circ}$ C. These coefficients of expansion were calculated with the expression $\alpha_{\text{avg}} = (L_t - L_{25}) / [L_{25}(t - 25)]$ in which L_t is the length at t° C, and L_{25} is the length at 25° C. The error of these average coefficients, estimated from repeated measurements, is about $\pm 3 \times 10^{-6}/^{\circ}$ C.

TABLE 2. Average coefficients of linear thermal expansion of Teflon in the annealed condition (sample A)

Temperature range °C	Coefficient of expansion per degree C
+25 to -190	86×10^{-6}
+25 to -150	96
+25 to -100	112
+25 to -50	135
+25 to 0	200
+25 to +50	124
25 to 100	124
25 to 150	135
25 to 200	151
25 to 250	174
25 to 300	218

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4. References

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