

Thermal Expansion Coefficient of Polytetrafluoroethylene in the Vicinity of Its Glass Transition at about 400°K.

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Synopsis

The linear thermal expansion of molded PTFE samples of various crystallinities was measured in the vicinity of the transition at about 400°K. In the plot of length of the specimen versus temperature, an inflection of the straight line was observed in the temperature range from 388 to 402°K., the mean value being 396°K. (123°C.) The change of the coefficient of linear thermal expansion at this temperature represents a typical feature of the second-order transition or the glass transition, designated as T_g . The ratio T_g/T_m is equal to 0.66, in accordance with the so-called $2/3$ -rule between the glass transition temperature (T_g) and the melting point (T_m) of many polymers. The coefficients of linear thermal expansion, below and above T_g , designated α_1 and α_2 respectively, increased with increasing amorphous fraction, A . The extrapolated values of α_1 and α_2 at $A = 0$ were both 0.6×10^{-4} deg.⁻¹, and those at $A = 1$ were 2×10^{-4} deg.⁻¹ and 3×10^{-4} deg.⁻¹, respectively. The value of $T_g \Delta\beta/A$, where $\Delta\beta = 3(\alpha_2 - \alpha_1)$, was approximately 0.12 which was closely in agreement with the value of 0.08 or 0.113 predicted by the theories for amorphous high polymers. From these experimental facts, it may be concluded that the transition of PTFE at about 400°K. is the glass transition which occurs in the amorphous region.

Introduction

In polytetrafluoroethylene (PTFE) there are two glass transitions: one at about 400°K. and the other at about 180°K. These transitions have been studied by the thermal expansion method,¹ x-ray diffraction,¹ rheological methods,²⁻³ and the dielectric method.⁹

Some authors have claimed that the transition at about 400°K. occurs in the amorphous region,⁶ but others contended that it occurs in the crystalline region.^{3-5,7-9}

In this paper, the results of thermal expansion measurements on a series of PTFE samples with different crystallinities and the influence of the crystallinity upon the thermal expansion coefficient are reported; the nature of the glass transition at 400°K. is also considered.

Samples and Experimental Procedure

The nine samples of PTFE powders used in this study (Table I) were commercial materials: Teflon (Du Pont), Fluon (Imperial Chemical Industries), and Polyflon (Daikin Kogyo). The process for the molding of

TABLE I
Thermal Expansion of PTFE

No.	Molded sample	Specific gravity (25°C./25°C.)	Amorphous fraction	T_g , °K.	$\alpha_1 \times 10^{-4}$ deg. ⁻¹	$\alpha_2 \times 10^{-4}$ deg. ⁻¹	$T_g \Delta\beta^a$	$T_g \Delta\beta/A$
1	Polyflon M-11A	2.1530	0.48	400	1.30	1.87	0.0684	0.143
2	Polyflon M-11	2.1624	0.45	397	1.24	1.62	0.0453	0.101
3	Fluon G1	2.1748	0.41	402	1.12	1.59	0.0567	0.138
4	Teflon 1	2.1763	0.41	398	1.22	1.57	0.0418	0.102
5	Teflon 7	2.1799	0.40	394	1.16	1.51	0.0414	0.103
6	Teflon 6C	2.1984	0.34	392	1.08	1.42	0.0400	0.118
7	Fluon CD1	2.2068	0.31	388	1.03	1.34	0.0361	0.116
8	Polyflon Fine	2.2258	0.26	397	0.93	1.11	0.0214	0.082
9	Teflon 6	2.2320	0.24	394	0.98	1.26	0.0331	0.138
				Mean 396				Mean 0.116

$$^a \Delta\beta = 3(\alpha_2 - \alpha_1).$$

test pieces from PTFE powders was as follows. About 30–50 g. of each powder was poured into a cylindrical mold cavity, 20 mm. in diameter. The mold charged with the powder was set in a vacuum vessel, where the pressure was reduced to about 1 mm. Hg. The piston was pushed down slowly onto the powder in the mold cavity. The preform pressure for the molding powders, samples 1, 2, 3, 4, and 5 in Table I, was 300 kg./cm², and that for the fine powders, samples 6, 7, 8, and 9, was 200 kg./cm.². The pressure was maintained for 20 min. in each case. The vacuum was intended to remove the air in the powder and to minimize the void content in the molded pieces.

After removal from the mold, the resulting preformed piece was heated up to 360°C. in an air oven at the rate of 44°C./hr., sintered at this temperature for 2 hr., and then cooled gradually to room temperature. The cooling rate was about 45°C./hr. in the temperature range 360–250°C., and was at a slower rate below 250°C.

The specific gravity of the molded pieces at 25°C. was determined in accordance with the procedures described in ASTM Designation D 792, Method A; the values are shown in Table I, arranged in the order of their magnitude.

Amorphous contents of the specimens were calculated from the measured values of specific gravity,^{10–12} assuming the void content was at zero, and they are shown in Table I.

Nine specimens of cylindrical shape, 10 mm. in diameter and 20 mm. in length, were prepared by machining these molded pieces and were used as specimens for the linear thermal expansion measurements in the direction of their axes.

The schematic diagram of the apparatus used in this experiment is shown in Figure 1. The specimen was maintained at desired temperatures by regulating the surrounding oil. The temperature of the oil around the

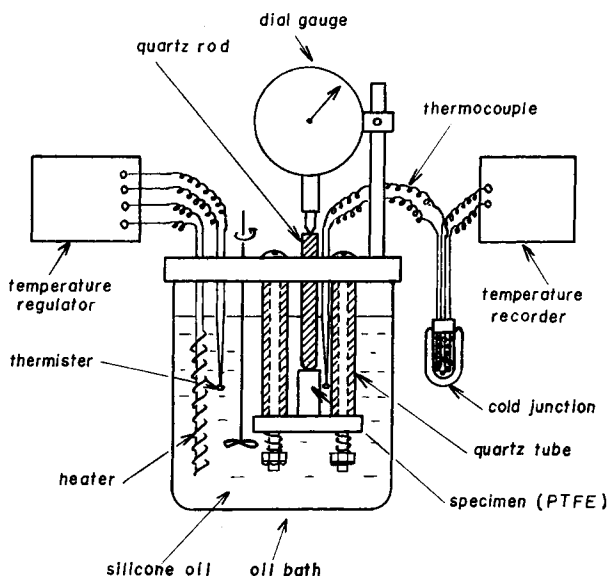


Fig. 1. Schematic diagram of the apparatus.

specimen was elevated stepwise in the range from 0 to 170°C., and the change in the length of the specimen with temperature was followed by means of the dial gage. The length became constant in about 20 min. at each temperature step.

Three times the coefficient of linear expansion was assumed to be that of cubical expansion, because the specimens prepared in such a free sintering method as mentioned above were confirmed to be isotropic in thermal expansion.¹³

Results and Discussion

An example of linear thermal expansion measurements is shown in Figure 2. In the plot of length versus temperature, a large jump and a smaller one appear at about 20°C. and 30°C., respectively, and an inflection of the straight line is seen at 124°C. (397°K.). From the slope of this curve, the coefficient of linear thermal expansion at each temperature was obtained as shown in Figure 2. The two peaks at about 20°C. and 30°C. on this curve represent the first-order transitions (the room temperature transition) as reported in the previous paper,¹⁴ while a step in the horizontal straight line at 124°C. represents a typical second-order transition, referred to as the glass transition temperature T_g .

The crystallinity of the pieces molded under these conditions varied considerably owing to properties of the powders. This might be due to the shape and the particle size of the powders as well as to their molecular weight. The specific gravity of the molded piece is known to vary according to the crystallinity and the void content. The influence of the void

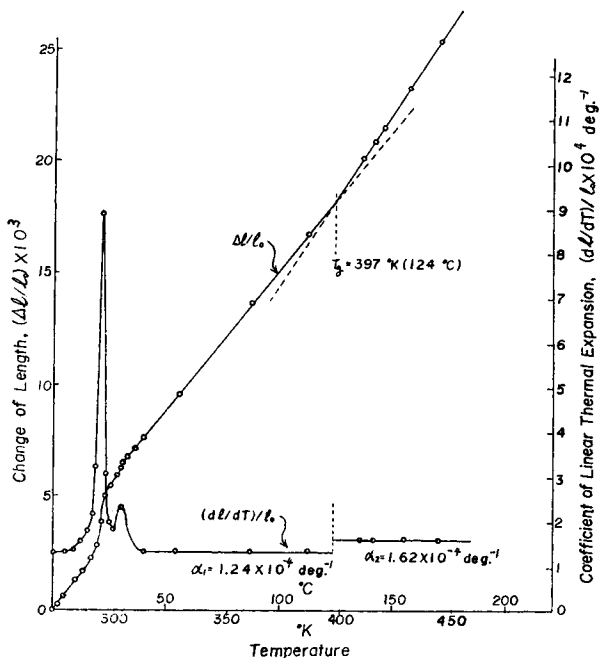


Fig. 2. Linear thermal expansion of PTFE (Polyfon M-11).

content upon the specific gravity in this experiment is assumed to be negligible, because the void content under these molding conditions is less than 0.5%. According to the results obtained by other authors,¹⁰ the molded Teflon 1 contained a void content of about 0.5% under molding conditions similar to those used in this experiment.

The glass transition temperature T_g of the nine specimens studied, varied in the range from 388°K. (115°C.) to 402°K. (129°C.), and the mean value was 396°K. (123°C.). No correlation between T_g and the crystallinity was found. As the melting point T_m of the molded PTFE is 600°K. (327°C.),¹⁵⁻¹⁷ the ratio T_g/T_m is equal to $2/3 \pm 0.02$, which agrees fairly well with the so-called $2/3$ -rule pointed out by Beaman,¹⁸ Jenckel,¹⁹ and Hirai.²⁰

α_1 and α_2 are the coefficients of linear thermal expansion below and above T_g , respectively, and they are given in Table I for the nine specimens. Plots of α_1 , α_2 , and $\Delta\alpha = \alpha_2 - \alpha_1$, against amorphous content are nearly on straight lines as shown in Figure 3. Both α_1 and α_2 tend to 0.6×10^{-4} deg.⁻¹ as extrapolated to zero point of amorphous content, increase with increasing amorphous content, and give the values of 2×10^{-4} deg.⁻¹ and 3×10^{-4} deg.⁻¹ respectively, as extrapolated to 100% of amorphous content. Consequently, $\Delta\alpha$, the difference between α_1 and α_2 , increases from zero to 1×10^{-4} deg.⁻¹ as the amorphous content increases. This fact means that the transition at about 400°K. occurs in the amorphous region.

There is a theory illustrating the relationship between T_g and $\Delta\beta$ of general amorphous high polymers, presented first by Hirai and Eyring,²¹

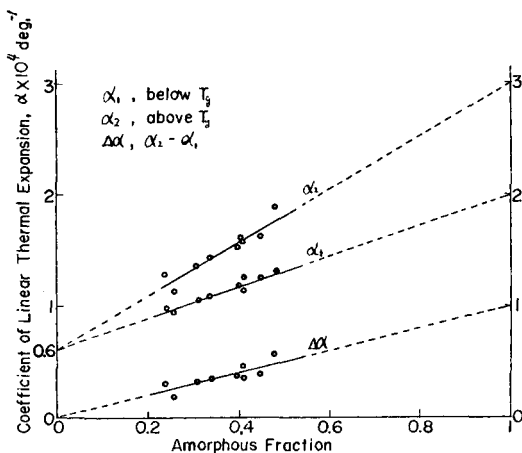


Fig. 3. Coefficient of linear thermal expansion vs. amorphous content of PTFE

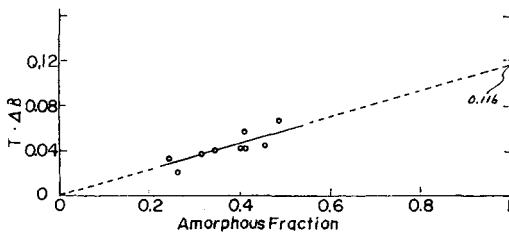


Fig. 4. $T_g \Delta\beta$ vs. amorphous content of PTFE.

and later by Simha and Boyer.²² According to these theories, the product, $T_g \Delta\beta$ is approximately equal to 0.08 or 0.113 for various amorphous high polymers, where $\Delta\beta$ is the difference between the coefficients of cubical expansion below and above T_g .

In partially crystallized molded PTFE, the magnitude of $T_g \Delta\beta$ divided by the amorphous fraction A , should correspond to that of $T_g \Delta\beta$ in amorphous high polymers. Plots of $T_g \Delta\beta$ against amorphous fraction in the nine specimens are given in Figure 4: they are roughly on a straight line, and the extrapolated value of 0.116 at $A = 1$ is closely in agreement with the theoretical values.

For the other glass transitions at 160°K., $\Delta\beta/A$ is about 7.0×10^{-4} deg.⁻¹,²² and so $T_g \Delta\beta/A$ is equal to 0.112, also in agreement with the theoretical value. The ratio of 180°K. and 293°K. (the room temperature transition) is about $2/3$.

This fact shows that the glass transition at 400°K. should correspond to the real melting temperature at 600°K., while the glass transition at 180°K. corresponds to the room temperature transition. This suggests that the higher glass transition may reflect the free rotation of each bond in the main chain in the amorphous regions, but the lower glass transition reflects smaller scale motion in the main chain in the amorphous regions.

References

1. Satokawa, T., and S. Koizumi, *Kogyo Kagaku Zasshi*, **65**, 1211 (1962).
2. Nohara, S., *Kobunshi Kagaku*, **14**, 318 (1957).
3. McCrum, N. G., *J. Polymer Sci.*, **34**, 355 (1959).
4. McCrum, N. G., *Makromol. Chem.*, **34**, 50 (1959).
5. Iller, K. H., and E. Jenckel, *Kolloid-Z.*, **165**, 84 (1959).
6. Becker, G. W., *Kolloid-Z.*, **167**, 44 (1959).
7. Eby, R. K., and K. M. Sinnott, *J. Appl. Phys.*, **32**, 1765 (1961).
8. Wada, Y., *J. Phys. Soc. Japan*, **16**, 1226 (1961).
9. Krum, F., and F. H. Müller, *Kolloid-Z.*, **164**, 81 (1959).
10. Thomas, P. E., J. F. Lontz, C. A. Sperati, and J. L. McPherson, *SPE J.*, **12**, 89 (1956).
11. Ryland, A. L., *J. Chem. Educ.*, **35**, 80 (1958).
12. Moynihan, R. E., *J. Am. Chem. Soc.*, **81**, 1045 (1959).
13. Yasuda, T., Y. Araki, and H. Suzuki, paper presented at the Debate Meeting on High Polymers, Osaka, October, 1958.
14. Yasuda, T., and Y. Araki, *J. Appl. Polymer Sci.*, **5**, 331 (1961).
15. McGeer, P. L., and H. C. Duus, *J. Chem. Phys.*, **20**, 1813 (1952).
16. Kuroda, T., *Repts. Gov. Ind. Res. Inst. Nagoya*, **5**, 257 (1956).
17. Kuroda, T., and H. Sakami, *Repts. Gov. Ind. Res. Inst. Nagoya*, **7**, 315 (1958).
18. Beaman, R. G., *J. Polymer Sci.*, **9**, 472 (1952).
19. Jenckel, E., *Kolloid-Z.*, **130**, 64 (1953).
20. Hirai, N., *J. Chem. Soc. Japan*, **74**, 445 (1953).
21. Hirai, N., and H. Eyring, *J. Polymer Sci.*, **37**, 51 (1959).
22. Simha, R., and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).

Résumé

L'expansion thermique linéaire de PTFE fondu, de cristallinités différentes a été mesurée au voisinage du point de transition à environ 400°K. Dans le graphique représentant la longueur de l'échantillon en fonction de la température, on a observé une inclinaison de la ligne droite dans le domaine de température allant de 388 à 402°K, la valeur moyenne étant 396°K (123°C). Le changement du coefficient d'expansion thermique linéaire à cette température représente une caractéristique typique de la transition de second ordre ou de la transition vitreuse, désignée par T_g (°K). Le rapport T_g/T_m est égal à 0.66, en accord avec la règle des $2/3$ entre la température de transition vitreuse (T_g) et le point de fusion (T_m) de plusieurs polymères. Les coefficients d'expansion thermique linéaire, en dessous et au dessus de T_g , désignés respectivement par α_1 et α_2 , augmentent lorsque la fraction amorphe, A , augmente. Les valeurs extrapolées de α_1 et α_2 pour $A = 0$ sont toutes les deux égales à $0.6 \times 10^{-4} \text{ deg.}^{-1}$ et celles pour $A = 1$ sont $2 \times 10^{-4} \text{ deg.}^{-1}$ et $3 \times 10^{-4} \text{ deg.}^{-1}$ respectivement. La valeur de $T_g \Delta\beta$ divisée par A , où $\Delta\beta = 3(\alpha_2 - \alpha_1)$ est approximativement égale à 0.12, ce qui est en parfait accord avec la valeur de 0.08 ou 0.113 prévue par les théories des polymères amorphes. Sur la base de ces résultats expérimentaux on peut conclure que la transition du PTFE aux environs de 400°K est la transition vitreuse qui a lieu dans la région amorphe.

Zusammenfassung

Die lineare thermische Ausdehnung von PTFE mit verschiedener Kristallinität wurde in der Umgebung des Umwandlungspunktes bei etwa 400°K gemessen. Bei der Kurve Probenlänge gegen Temperatur wurde im Temperaturbereich von 388 bis 402°K eine Krümmung der geraden Linie beobachtet, deren Zentrum bei 396°K (123°C) lag. Die Änderung des linearen thermischen Expansionskoeffizienten bei dieser Temperatur bildet ein typisches Merkmal der Umwandlung zweiter Ordnung oder der Glasumwandlung, bezeichnet als T_g (°K). Das Verhältnis T_g/T_m beträgt 0,66, im Übereinstimmung

mit der sogenannten $2/3$ -Regel für die Glasumwandlungstemperatur T_g und den Schmelzpunkt T_m vieler Polymerer. Der lineare thermische Expansionskoeffizient, oberhalb und unterhalb T_g als α_1 bzw. α_2 bezeichnet, nimmt mit steigendem amorphen Anteil, A , zu. Die extrapolierten Werte von α_1 und α_2 bei $A = 0$ betragen beide $0,6 \times 10^{-4} \text{ grad}^{-1}$ und diejenigen bei $A = 1$ betragen $2 \times 10^{-4} \text{ grad}^{-1}$ bzw. $3 \times 10^{-4} \text{ grad}^{-1}$. $T_g \Delta\beta$ gebrochen durch A , wo $\Delta\beta = 3(\alpha_2 - \alpha_1)$, hatte in enger Übereinstimmung mit den von den Theorien für amorphe Hochpolymere geforderten Werten von 0,08 oder 0,113 einen Wert von 0,12. Aus diesen Versuchsergebnissen kann geschlossen werden, dass die Umwandlung von PTFE bei etwa 400°K die Glasumwandlung ist, welche im amorphen Bereich vor sich geht.

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