

First-Order and Second-Order Transitions of Polytetrafluoroethylene in the Temperature Range of 80–140° C. Measured by Several Methods

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Synopsis

Transitions of polytetrafluoroethylene (PTFE) have been studied through the measurements of thermal expansion coefficient, compressive Young's modulus, dynamic modulus and loss tangent, and dielectric loss tangent and dielectric constant by a Schering bridge, in the temperature range of 50–170°C. On the curves of linear thermal expansion coefficient versus temperature, two small peaks were observed at about 80 and 100°C., and two steps at about 120 and 140°C. for several specimens of PTFE with different crystallinities. These two peaks and two steps are thought to mean two first-order transitions and two second-order transitions, respectively. Static compressive Young's modulus, dynamic shear modulus by a torsion pendulum method, and dielectric constant by a Schering bridge plotted against temperature illustrated irregular changes at about 80, 100, 120, and 140°C. These four irregular changes correspond to four transitions observed by the thermal expansion method. Plots of dynamic loss tangent and dielectric loss tangent against temperature illustrated four dispersions or irregular changes at about 80, 100, 120, and 140°C.; specimens with higher crystallinities seem to show larger changes at about 80 and 100°C., and smaller changes at about 120 and 140°C. than those with lower crystallinities. According to these measurements, it is concluded that in PTFE there exist two first-order transitions at about 80 and 100°C. and two second-order transitions at about 120 and 140°C.; this is the same as concluded from the previous stress relaxation study.

INTRODUCTION

In the previous paper,¹ it was reported that two first-order transitions and two second-order transitions for molded polytetrafluoroethylene (PTFE) were observed in the temperature range between 80 and 130°C. by using the stress relaxation method. In addition to the stress relaxation method, other methods were used thereafter for observation of the transitions in the same temperature range. The methods were measurements of coefficient of linear thermal expansion, dynamic viscoelastic properties by a torsion pendulum, static compressive Young's modulus, and dielectric properties by a Schering bridge. In each method, four transitions were found in the same temperature regions as were observed by using the stress relaxation method. The reliability of the stress relaxation method was recognized by other different methods, which will be summarized as follows.

LINEAR THERMAL EXPANSION

The thermal expansion study on this polymer in the vicinity of its glass transition temperature at about 130°C. was reported previously.² In that study only one transition which was thought to occur in the amorphous region was observed at about 130°C. Because more accurate apparatus was used in this study and more temperature points were used than in the previous thermal expansion study,² multiple transitions may have been found.

Experimental Procedure

The measurements in this paper were carried out carefully and the apparatus was improved in accuracy. The change in length of the cylindrical specimen, 15 mm. in diameter and 40 mm. in length, was followed by means of a strain gauge of unbonded type with a capacity of ± 0.82 mm. full-scale strain and with the sensibility of 2.6 mv./mm. at 1 v. input voltage and was recorded electrically. The temperature of the specimen was elevated stepwise in the range of 50–170°C. and the length became constant in about 20 min. at each temperature step. The length of the specimen was taken at each temperature after it became constant, and the measurements were made at more temperature steps than in the previous study.²

Results and Discussion

An example of linear thermal expansion is shown in Figure 1. In the plots of length change against temperature, two jumps at about 85 and 100°C., and two inflections at about 120 and 140°C. may be seen. In other words, on the curve of coefficient of linear thermal expansion versus temperature, two peaks and two steps appear at about 85, 100, 120, and 140°C., respectively. The two changes at about 85 and 100°C. represent a typical feature of first-order transitions, and the other two changes at about 120 and 140°C. a typical feature of second-order transitions.

Relations between coefficient of linear thermal expansion and temperature are illustrated in Figure 2 for various specimens with different crystallinities measured by the density method.³⁻⁶ In these examples two types of changes are seen as are shown in Figure 1, though only one first-order change appears in a specimen with comparatively lower crystallinity, 52%, and only one second-order change in a case of higher crystallinity, 81%.

In Figure 3, linear thermal expansion coefficients above and below the two second-order changes, α_1 and α_3 , respectively, and the differences between the two, $\Delta\alpha = \alpha_1 - \alpha_3$, are plotted against amorphous fraction A measured by the density method.³⁻⁶ In this figure, the extrapolated values of α_1 and α_3 at $A = 0$ were both $0.6 \times 10^{-4} \text{ }^\circ\text{C.}^{-1}$, and those at $A = 1$ were 3.52×10^{-4} and $2.44 \times 10^{-4} \text{ }^\circ\text{C.}^{-1}$, respectively. Consequently, the value of $T_g\Delta\beta$ divided by A , where $\Delta\beta$ is $3(\alpha_1 - \alpha_3)$ and T_g is the absolute temperature of the transition, was approximately 0.13, which

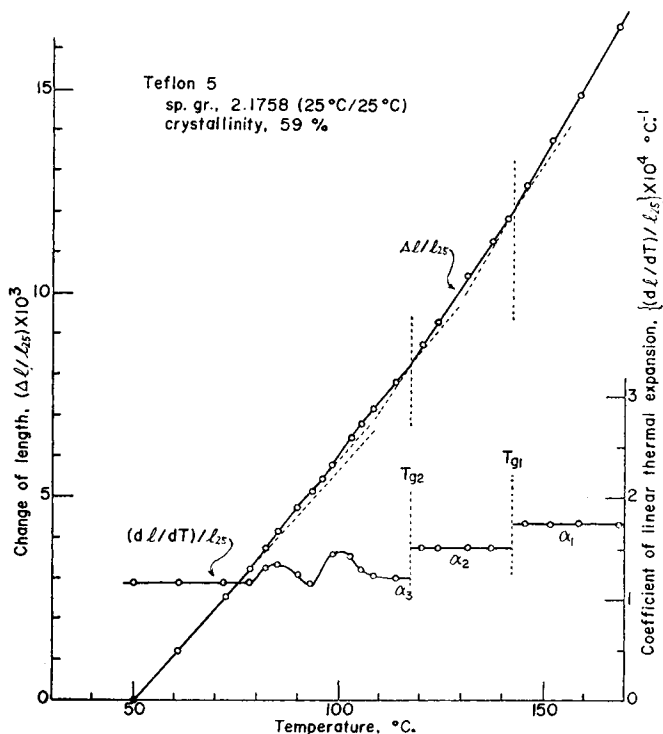


Fig. 1. Linear thermal expansion of polytetrafluoroethylene (Teflon 5).

is closely in agreement with the value of 0.08 or 0.112 predicted by the theories for amorphous high polymers.^{7,8} This value, 0.13, is approximately equal to that obtained similarly in the previous study,² 0.12. The two second-order transitions at about 120 and 140°C. are thought to be of the same class and belong to the transition at 130°C. which has appeared in many papers.^{2,9-18}

DYNAMIC VISCOELASTIC PROPERTIES BY THE TORSION PENDULUM METHOD

Experimental Procedure

The method in this study is similar to that used by McCrum.¹⁹ Two ribbonlike specimens, about 1 mm. in thickness, 10 mm. in width, and 80 mm. in length, shaved from molded Teflon 5, were used in the measurements. The crystallinities of the specimens were 47 and 57% measured by the density method.³⁻⁶ In the apparatus, the specimen was held rigidly at the top by the upper clamp and attached by the lower clamp to the inertia arm, 42.9 g. in weight and 3.08×10^3 g.-cm.² in moment of inertia. When the upper clamp was given a one-time movement of a small angle at the equilibrium state of the pendulum and then fixed, the pendulum performed

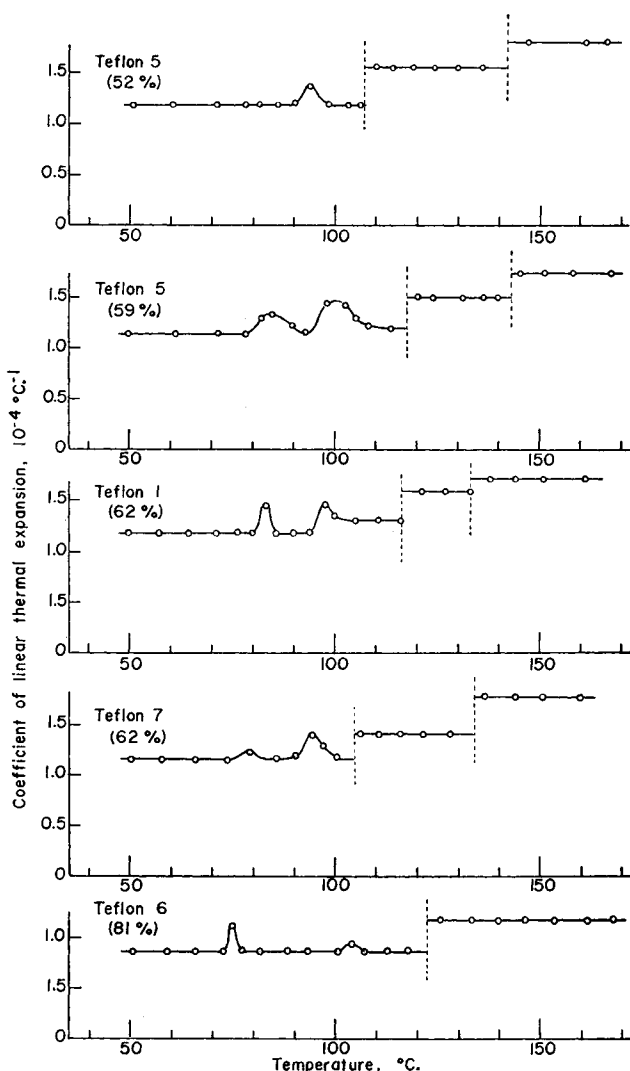


Fig. 2. Coefficient of linear thermal expansion vs. temperature for polytetrafluoroethylene (Teflon 1, 5, 6 and 7).

torsional oscillations around the vertical axis of the specimen. The pendulum assembly was set in an air bath, the air in which was kept at an arbitrary temperature uniformly within $\pm 0.1^\circ\text{C}$. by a thermostat of an electric heater and a fan. Prior to each measurement, the air in the bath was kept at the measuring temperature. The same specimen was used for a series of measurements at different temperatures in the range from 60 to 150°C . at 5°C . increments. Both the period and decay of the oscillations were measured by observing the oscillations of a light beam reflection from a mirror attached to the inertia arm by means of a galva-

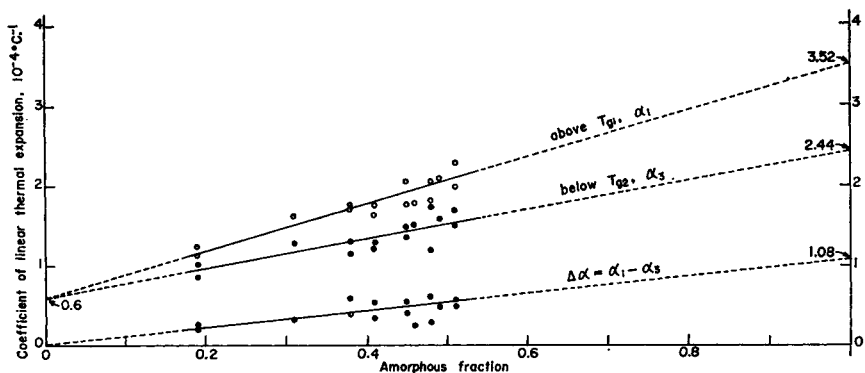


Fig. 3. Coefficient of linear thermal expansion vs. amorphous content for polytetrafluoroethylene in the transition region at about 130°C.

nometer lamp-and-scale. The period in the range of 60–150°C. was about 1–3 sec.

Results and Discussion

Assuming the Voigt model, dynamic shear modulus and dynamic loss tangent were obtained (Fig. 4). Irregular changes on the curves of dynamic shear modulus for the two specimens, appear at about 80, 100,

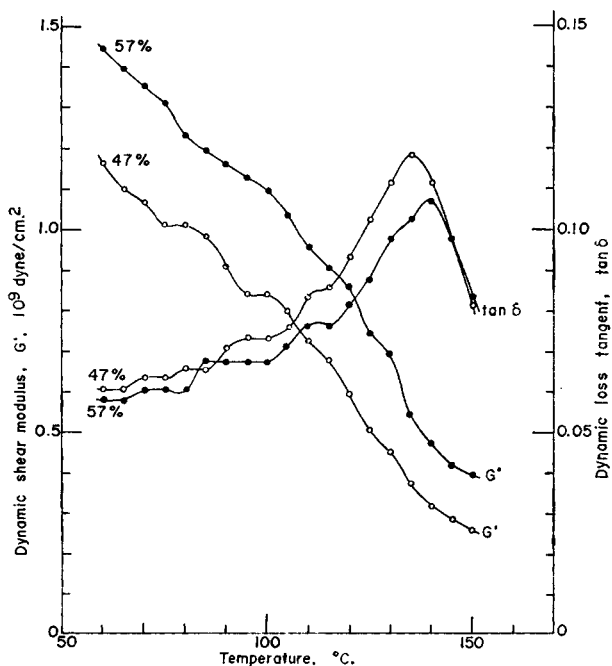


Fig. 4. Dependence of viscoelastic properties of polytetrafluoroethylene (Teflon 5) on temperature in the torsion pendulum method.

120, and 130°C. On the curves of dynamic loss tangent, three steps at about 75, 90, and 110°C., and a peak at about 140°C. are shown. These irregular changes in viscoelastic properties at about 80, 100, 120, and 140°C. correspond to those observed by the thermal expansion method and by the stress relaxation method.¹

STATIC COMPRESSIVE YOUNG'S MODULUS

Compressive relaxation moduli at 6 sec. after compression in the previous study,¹ are plotted against temperature in Figure 5. In this figure the results for three specimens with different crystallinities, by the density method,³⁻⁶ are shown. On these curves, remarkable changes of Young's

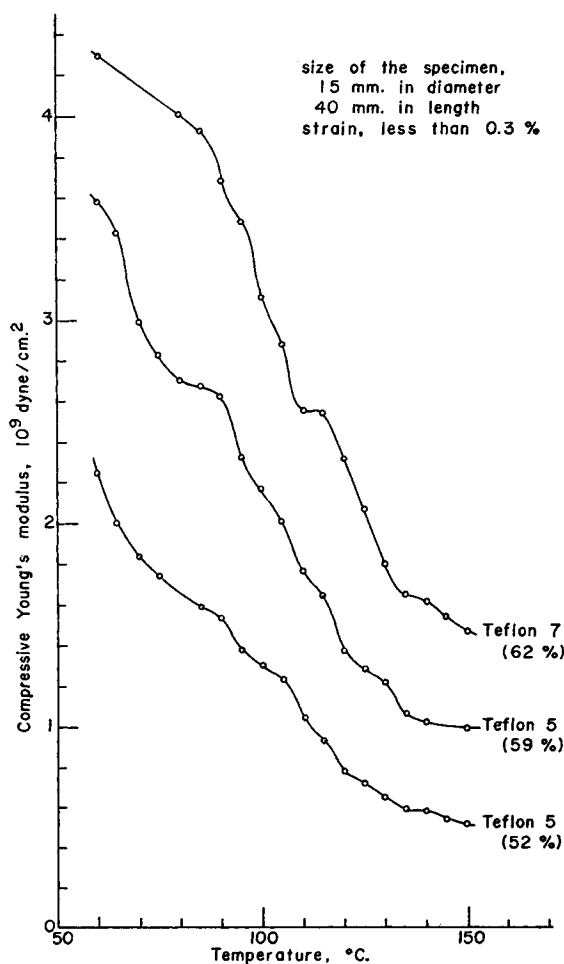


Fig. 5. Young's modulus at 6 sec. after compression for polytetrafluoroethylene samples of different crystallinities plotted against temperature.

moduli can be seen at about 80, 100, 120, and 130°C.; these changes are thought to correspond to four transitions observed in the stress relaxation method.¹

DIELECTRIC PROPERTIES MEASURED BY THE SCHERING BRIDGE METHOD

Dielectric loss tangent $\tan \delta$ and dielectric constant ϵ' for PTFE sheets were measured by the Schering bridge method²⁰ at a frequency of 50

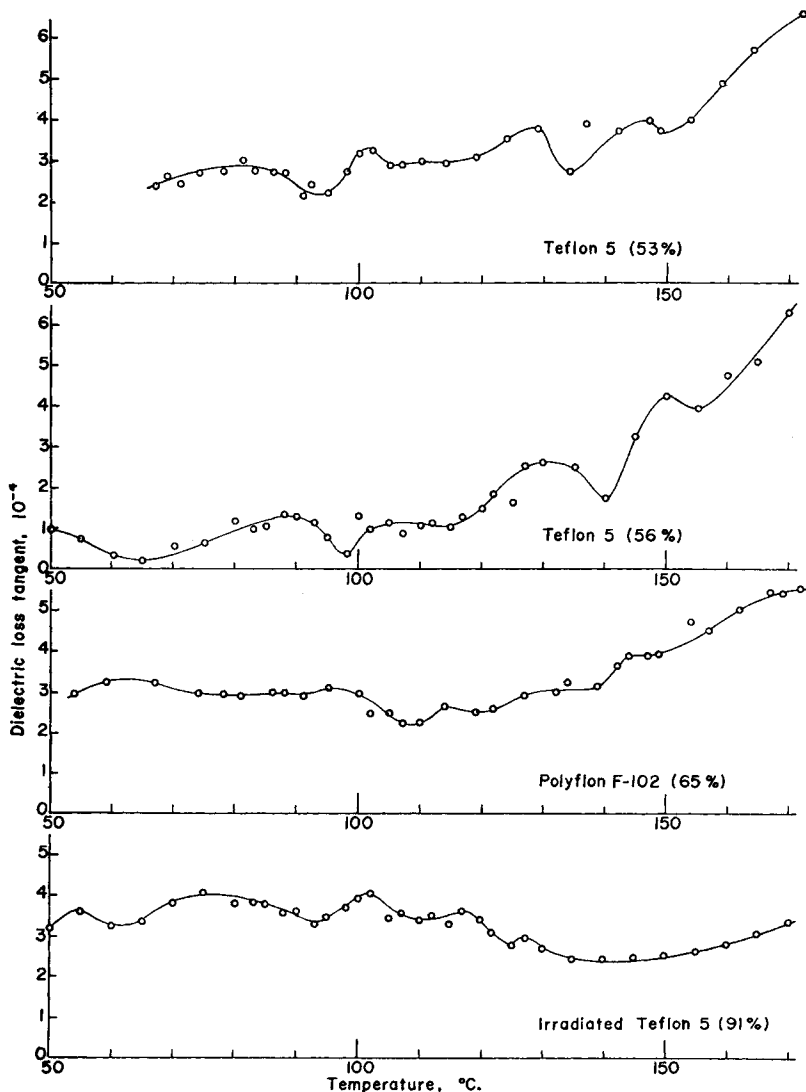


Fig. 6. Plots of dielectric loss tangent against temperature in the range of 50–170°C. for several specimens of polytetrafluoroethylene (Schering bridge, 50 cycle/sec.)

cycle/sec. The specimens were circular sheets, about 8 cm. in diameter and 0.2 mm. in thickness. A pair of circular electrodes, 56 mm. (guarded) and 70 mm. (unguarded) in diameter, and a guard ring, 60 mm. in inside diameter and 70 mm. in outside diameter, were made by painting films of

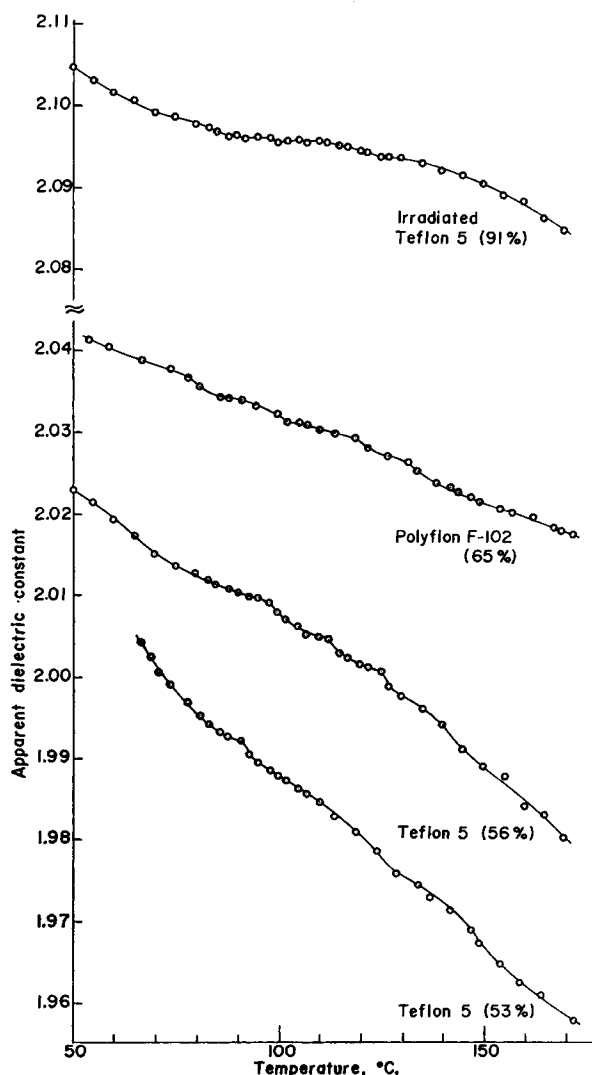


Fig. 7. Plots of dielectric constant against temperature in the range of 50–170°C. for several specimens of polytetrafluoroethylene (Schering bridge, 50 cycle/sec.).

conductive paint on both sides of the specimen. The electrode assembly was set in a small air bath, the air in which was kept at an arbitrary measuring temperature within $\pm 0.1^\circ\text{C}$. A series of measurements were made at different temperatures in the range from 50 to 170°C. in ascending order.

Each measurement was carried out at about 5 min. after the temperature reached a constant at each step.

Examples of the results are given in Figures 6 and 7, where $\tan \delta$ and ϵ' are plotted against temperature for specimens with different crystallinities. On $\tan \delta$ -temperature curves in Figure 6 broad peaks are illustrated at about 80, 100, 130, and 150°C., and in Figure 7 irregular changes of ϵ' are shown at the same temperature regions. The shape of $\tan \delta$ curves in Figure 6 are similar to those of the dynamic loss tangent curves in Figure 4. Irregular changes of $\tan \delta$ and ϵ' at about 80 and 100°C. seem to be more obvious for specimens with higher crystallinities, and on the other hand those at about 130 and 150°C. appear to be more remarkable for specimens with lower crystallinities.

CONCLUSION

In the measurements of linear thermal expansion for PTFE in the temperature range of 50–170°C., two first-order transitions at about 80 and 100°C., and two second-order transitions at about 120 and 140°C. were observed.

These four transitions were also illustrated as four irregular changes on the curves of static Young's modulus, dynamic shear modulus, and dielectric constant at about 80, 100, 120, and 140°C. The dielectric and dynamic methods showed four dispersions, or irregular changes, on the curves of dielectric loss tangent and dynamic loss tangent versus temperature, at the same temperature regions.

The present study showed the existence of four transitions in PTFE at about 80, 100, 120, and 140°C. The same conclusion was obtained as in the previous study of the stress relaxation for the same polymer.

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Résumé

On a étudié les transitions présentées par le polytétrafluoroéthylène (PTFE) dans le domaine de température compris entre 50 et 170°C, en mesurant le coefficient de dilatation thermique, le module de compression de Young, le module et l'angle de perte dynamiques, l'angle de perte diélectrique et la constante diélectrique (par un pont de Schering). Sur les courbes représentant l'évolution du coefficient de dilatation thermique linéaire en fonction de la température, on peut observer deux petits pics vers 80 et 100°C et deux paliers vers 120 et 140°C pour divers échantillons de PTFE de cristallinités différentes. On suppose que ces deux pics et ces deux paliers correspondent respectivement à deux transitions de premier ordre et à deux transitions de second ordre. Le module de compression statique de Young, le module de cisaillement dynamique (mesuré par la méthode au pendule de torsion) et la constante diélectrique (mesurée par un pont de Schering), ont été portés graphiquement en fonction de la température et l'on constate une évolution irrégulière aux environs de 80, 100, 120, et 140°C. Ces quatre irrégularités correspondent aux quatre transitions observées par la méthode de dilatation thermique. En portant l'angle de perte dynamique et l'angle de perte diélectrique en fonction de la température, on constate quatre irrégularités vers 80, 100, 120, et 140°C. Il semble que les échantillons de cristallinité plus élevée présente des variations plus importantes à 80 et 100°C et plus faibles à 120 et 140°C que les échantillons de faible cristallinité. Ces mesures, permettent de conclure que pour le PTFE, il existe deux transitions de premier ordre situées à 80 et 100°C et deux transitions de second ordre situées à 120 et 140°C. Ceci rejoint les conclusions tirées précédemment des études de relaxation de la tension.

Zusammenfassung

Die Umwandlung von Polytetrafluoräthylene (PTFE) wurde mittels Messung des thermische Ausdehnungskoeffizienten, des Young-Kompressionsmoduls, des dynamischen Moduls und des Verlusttangens sowie des dielektrischen Verlusttangens und der Dielektrizitätskonstante mit einer Scheringbrücke im Temperaturbereich von 50–170°C untersucht. Auf der Kurve für den linearen thermischen Ausdehnungskoeffizienten gegen die Temperatur wurden bei etwa 80 und 100°C zwei kleine Maxima beobachtet und bei etwa 120 und 140°C zwei Stufen für mehrere PTFE-Proben mit verschiedener Kristallinität. Diese beiden Maxima und die beiden Stufen bedeuten wahrscheinlich zwei Umwandlungen erster Ordnung bzw. zwei solche zweiter Ordnung. Beim Auftragen des statischen Young-Kompressionsmodul, des dynamischen Schubmoduls nach einer Torsionspendelmethode und der Dielektrizitätskonstanten mittels Scheringbrücke gegen die Temperatur werden irreguläre Änderungen bei etwa 80, 100, 120, und 140°C beobachtet. Diese vier irregulären Änderungen entsprechen den vier nach der thermischen Expansionsmethode beobachteten Umwandlungen. Auftragung des dynamischen Verlusttangens und des dielektrischen Verlusttangens gegen die Temperatur zeigt vier Dispersionsgebiete oder irreguläre Änderungen bei etwa 80, 100, 120, und 140°C; Proben mit höherer Kristallinität scheinen grössere Änderungen bei etwa 80 und 100°C und kleinere bei etwa 120 und 140°C zu zeigen als solche mit niedrigerer Kristallinität. Diese Messungen führen zu dem Schluss, dass in PTFE zwei Umwandlungen erster Ordnung bei etwa 80 und 100°C und zwei Umwandlungen zweiter Ordnung bei etwa 120 und 140°C bestehen, was den früher aus Spannungsrelaxation-untersuchungen gezogenen Schlüssen entspricht.

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