

Second-Order Transitions of Polytetrafluoroethylene at about -30°C . Measured by Several Methods

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Synopsis

Measurements of compressive stress relaxation, linear thermal expansion, and dielectric properties were carried out for molded polytetrafluoroethylene (PTFE) in the temperature range of -60 to 10°C . In the measurements of stress relaxation over the range -55 to 5°C ., at 5°C . intervals, a master curve was obtained with good overlapping from a series of stress relaxation curves made from the same specimen at different temperatures, by application of the so-called Ferry's reduction method. The reduction factor a_T at different temperatures was plotted in logarithmic scale against the reciprocals of the absolute temperatures, and a diagram of the apparent activation energy versus temperature was obtained from the slope of the $\log a_T$ versus $1/T$ curve. There existed two sharp maxima at about -40 and -15°C . in the diagram of the apparent activation energy. Compressive relaxation moduli at a definite time after compression were plotted against temperature, and on the curve remarkable changes of Young's modulus were illustrated at about -40 and -15°C . On the curve of coefficient of linear thermal expansion versus temperature, two steps were observed at about -40 and -15°C . for several specimens of PTFE with different crystallinities. The value of $T_g/3(\alpha_1 - \alpha_3)/A$ was about 0.04, where T_g is the mean value of the two transition temperatures (absolute), α_1 and α_3 are coefficients of linear thermal expansion above and below the two transitions, and A is the amorphous fraction of each specimen. Plots of dielectric loss tangent $\tan \delta$ and dielectric constant ϵ' measured by a Schering bridge at a frequency of 50 cycle/sec. against temperature gave two dispersions of $\tan \delta$ at about -35 and -25°C ., and two irregular changes of ϵ' at the same temperature regions. According to these measurements, it is concluded that in PTFE two second-order transitions occur at about -40 and -15°C . The mean value of the two transition temperatures in absolute scale, 245°K . (-28°C .), is nearly equal to two-thirds of the first-order transition temperature at about 363°K . (90°C .).

INTRODUCTION

In polytetrafluoroethylene (PTFE) various transitions have been found. They are three kinds of first-order transitions at about 33 ,¹⁻³ 90 ,^{4,5} and 20°C .,^{2,3,6-19} and three kinds of second-order transitions at about 130 ,^{4,5,20-31} -30 ,^{25,29,30} and -90°C .^{21-25,27,29,32,33} These three kinds of second-order transitions exist at two-thirds the absolute temperatures of the three kinds of first-order transitions; i.e., the so-called two-thirds rule³⁴⁻³⁶ seems to be applicable to the three pairs of first- and second-order transitions. Most transitions of PTFE appear in closely spaced doublets, e.g., a pair of second-order transitions at about 120 and 140°C .,^{4,5} a pair

of first-order transitions at about 80 and 100°C.,^{4,5} and room-temperature transitions at 20 and 30°C.^{2, 3, 7, 8, 10-14, 16, 18, 19}

The transition at about -30°C. can be seen in the experiments of a few earlier papers,^{25,29} and in recent years it has been observed by Ohzawa and Wada.³⁰ However, it was observed not as a double but as a single transition. In separation of multiple transitions of high polymers, measuring methods of long time scale are effective; these have been mentioned in the previous paper,^{4,5} and are stress relaxation, thermal expansion, and dynamic or dielectric methods used at lower frequencies.

This paper deals with some results of measurements of the transitions of PTFE at about -30°C. by means of stress relaxation, linear thermal expansion and dielectric methods.

STRESS RELAXATION

Experimental Procedure

The apparatus and procedure used in the present study were almost the same as were described in detail in a previous paper.⁴ The same specimen, a cylinder 15 mm. in diameter and 40 mm. in length, was used for a series of measurements at thirteen different temperatures in the range from 5 to -55°C. at 5°C. decrements. Each measurement was carried out once in 24 hr., and the total strain given to the specimen in every measurement did

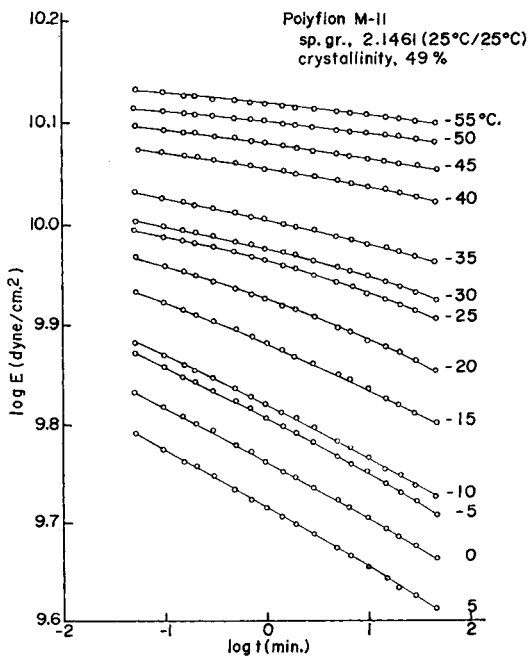


Fig. 1. Stress relaxation curves of polytetrafluoroethylene (Polyflon M-11) between -55 and 5°C.

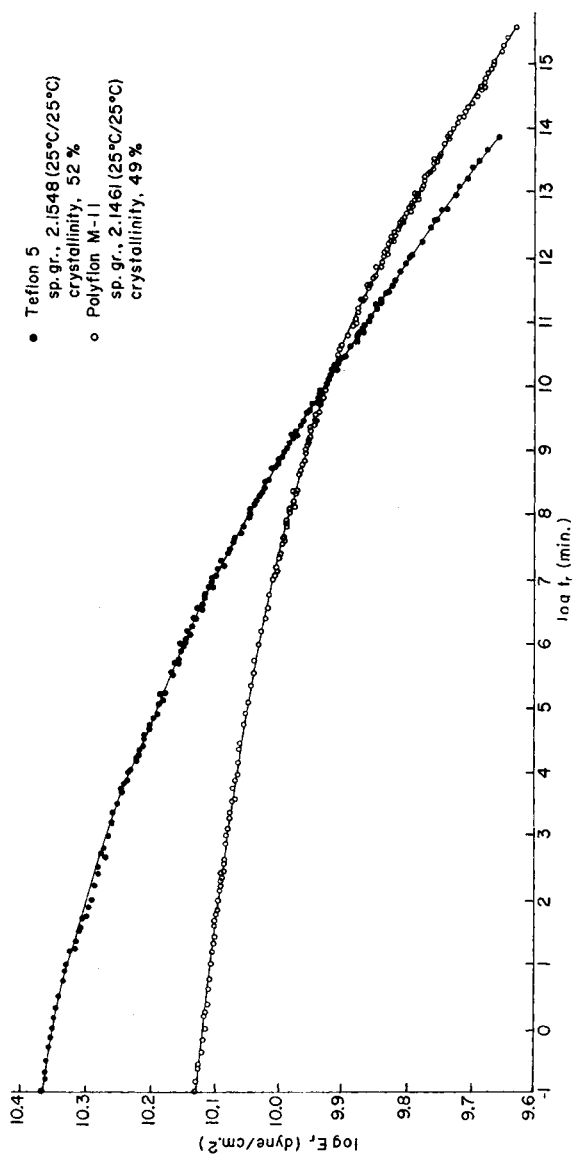


Fig. 2. Stress relaxation master curves of polytetrafluoroethylene (Teflon 5 and Polyflon M-11) reduced to -55°C .

not exceed 0.4% (0.16 mm.). The temperature-regulating device for the specimen was remodeled so that methanol, cooled at an arbitrary temperature by Dry Ice, was circulated around the specimen.

Results and Discussion

Several series of stress relaxation curves were obtained, an example of which is shown in Figure 1. As is shown in Figure 2, a master curve for a specimen was then obtained with good overlapping by the application of

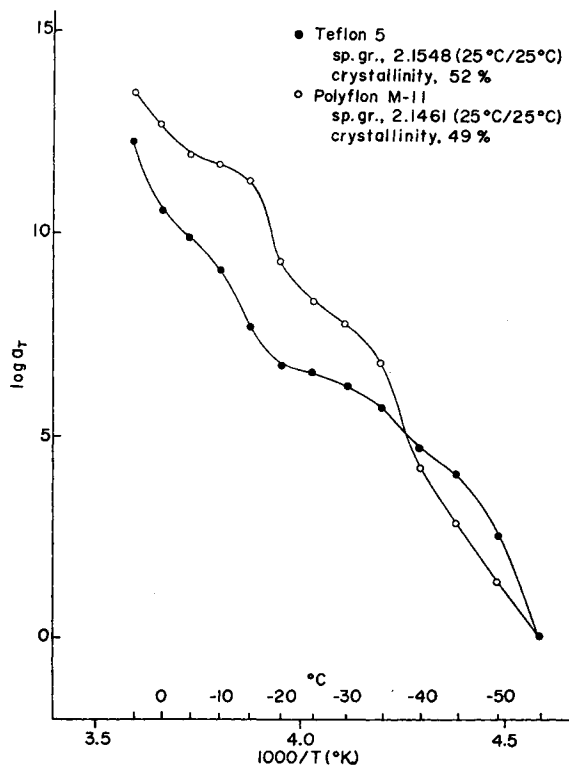


Fig. 3. Relation between Ferry's reduction factor a_T and temperature for polytetrafluoroethylene (Teflon 5 and Polyflon M-11).

Ferry's reduction method,^{16,18,39} which consists of shifting these curves along the time axis so as to overlap each other.

Figure 3 shows the reduction factor a_T at different temperatures plotted on a logarithmic scale against the reciprocals of the absolute temperatures $1/T$ for two specimens. From the slope of the curves (Fig. 3) at each temperature, assuming the reduction factor a_T to be in accordance with the Arrhenius equation, the relations between the apparent activation energy and temperature were obtained for the two specimens, which are illustrated in Figure 4. As is clearly seen in Figure 4, there are two sharp maxima at

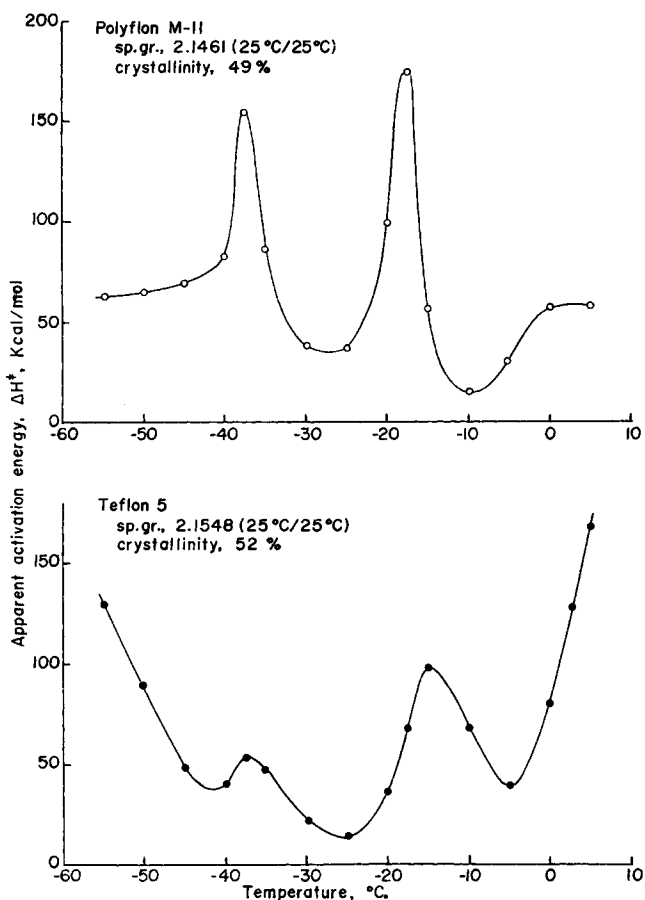


Fig. 4. Relation between the apparent activation energy ΔH^\ddagger of Ferry's reduction factor a_T and temperature in the method of stress relaxation for polytetrafluoroethylene (Polyflon M-11 and Teflon 5).

about -40 and -15°C ., which may mean two second-order transitions in those temperature regions.

Compressive relaxation moduli at 0.1, 1, and 10 min. after compression are plotted against temperatures in Figure 5. In this figure the results for two specimens with different crystallinities, by the density method, are shown. On these curves, remarkable changes of Young's moduli can be seen at about -40 and -15°C .; these changes are thought to correspond to the two transitions observed at the same temperatures in the stress relaxation method.

LINEAR THERMAL EXPANSION

Experimental Procedure

The method of measurement in this paper was the same as was used in the previous study.⁵ The change in length of a cylindrical specimen 15

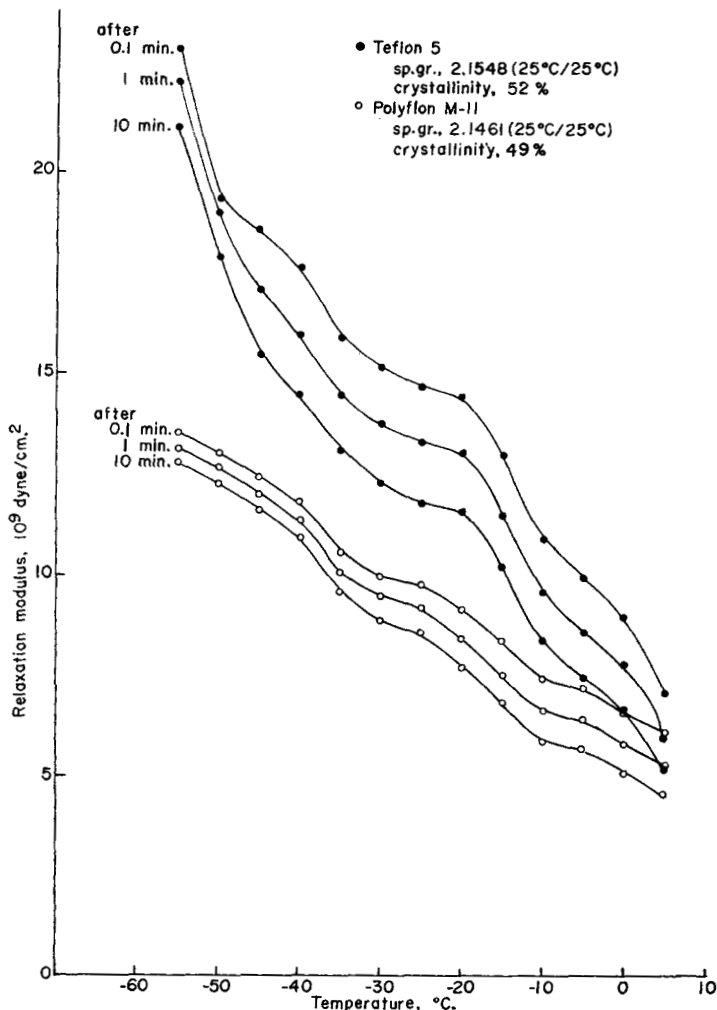


Fig. 5. Plots of compressive relaxation modulus against temperature for polytetrafluoroethylene (Teflon 5 and Polyflon M-11).

mm. in diameter and 40 mm. in length, due to thermal expansion, was followed by means of a strain gage and recorded electrically. Temperature regulation was made by circulating methanol, cooled at an arbitrary temperature by Dry Ice, around the specimen case. The temperature of the specimen was decreased stepwise in the range from 10 to $-55^{\circ}\text{C}.$, and at each temperature step a measurement of length change was made.

Results and Discussion

Examples of linear thermal expansion are shown in Figure 6, where double inflections may be seen at about -40 and $-15^{\circ}\text{C}.$ on the length change versus temperature curve, and two steps may be seen at those

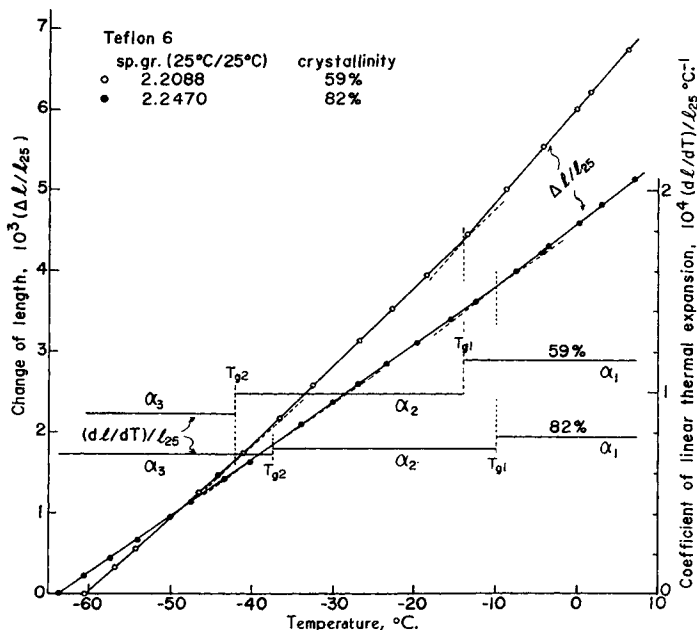


Fig. 6. Linear thermal expansion for polytetrafluoroethylene samples of different crystallinities (Teflon 6).

temperatures on the thermal expansion coefficient versus temperature curve. Figure 7 illustrates coefficient of linear thermal expansion versus temperature for several specimens with different crystallinities. Double steps may be seen at about -40 and -15°C . on thermal expansion coefficient-temperature curves. These steps represent a feature of second-order transitions.

In Figure 8, linear thermal expansion coefficients above and below these 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 which was measured by the density method.^{15,17,40,41} In this figure, the extrapolated values of α_1 and α_3 at $A = 0$ were both 0.5×10^{-4} , and those at $A = 1$ were 1.94×10^{-4} and $1.40 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$, respectively. Consequently, the value of $T_g \Delta\beta/A$, where $\Delta\beta$ is $3(\alpha_1 - \alpha_3)$ and T_g is the mean value of absolute temperatures of the two transitions, was approximately 0.04, which is smaller than the value of 0.08 or 0.112 predicted by the theories for amorphous high polymers.^{37,38}

DIELECTRIC PROPERTIES

Experimental Procedure

Dielectric loss tangent $\tan \delta$ and dielectric constant ϵ' for PTFE sheets were measured by the Schering bridge method⁴² at a frequency of 50 cycle/sec. The specimens were circular sheets, about 8 cm. in diameter

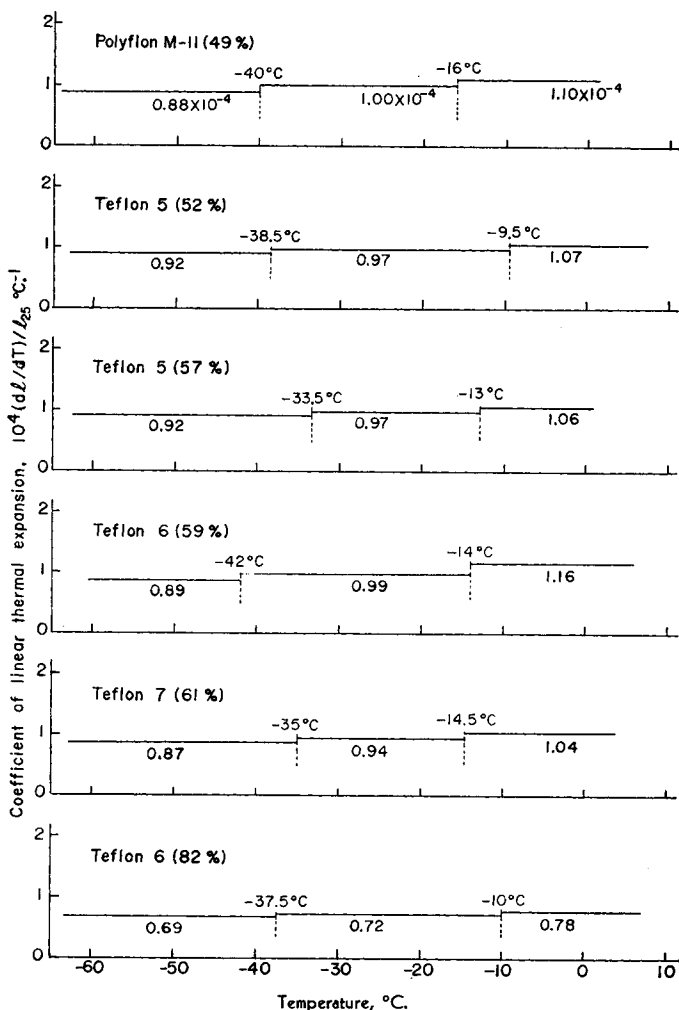


Fig. 7. Coefficient of linear thermal expansion vs. temperature for polytetrafluoroethylene (Polyflon and Teflon).

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 conductive paint on both sides of the specimen. The electrode assembly was set in a metallic liquid-proof vessel, in which a electric heater was fixed for precise temperature regulation of the specimen. The liquid-proof vessel was dipped in a bath of methanol cooled by Dry Ice, the temperature of which was kept at about $10^{\circ}\text{C}.$ below each measuring temperature. The temperature around the specimen was regulated at an arbitrary temperature within $\pm 0.1^{\circ}\text{C}.$ by the electric heater in the vessel. A series of measurements was made at different temperatures in the range from 10

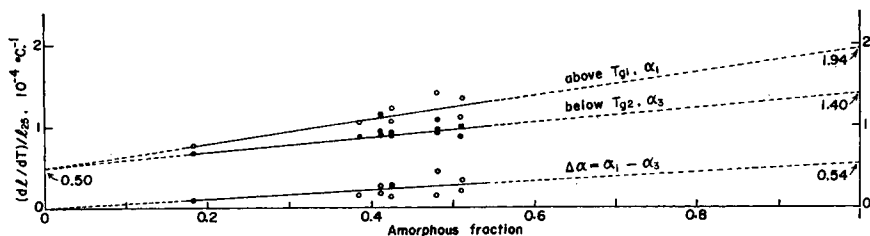


Fig. 8. Coefficient of linear thermal expansion vs. amorphous content for polytetrafluoroethylene in the transition region at about -30°C .

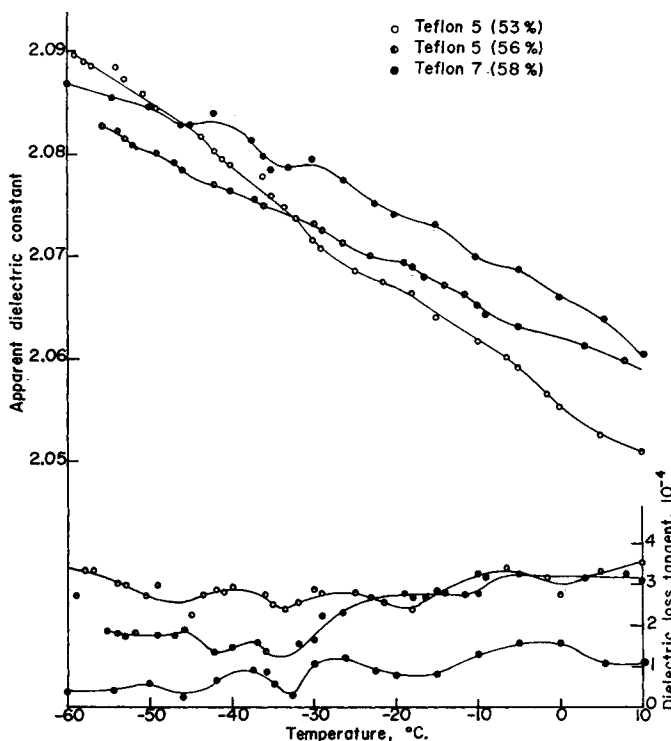


Fig. 9. Dielectric properties vs. temperature in the range of -60 to 10°C . for several specimens of polytetrafluoroethylene (Schering bridge, 50 cycle/sec.).

to -60°C . in descending order. Each measurement was carried out at about 5 min. after the temperature reached a constant for each step.

Results and Discussion

Examples of the results are given in Figure 9, where $\tan \delta$ and ϵ' are plotted against temperature for specimens with different crystallinities. On the curves of $\tan \delta$ two peaks are shown at about -35 and -25°C ., and on the curves of ϵ' irregular changes are illustrated at the same temper-

ature regions for each specimen. The two dispersions of $\tan \delta$ and irregular changes of ϵ' are thought to correspond to the two second-order transitions at about -40 and -15°C . observed by the other methods.

CONCLUSION

In the measurements of stress relaxation, linear thermal expansion, and dielectric properties for molded PTFE in the temperature range of -60 to 10°C ., two second-order transitions were observed at about -40 and -15°C . These two transitions probably belong to the same class as the other doublet transitions of this polymer, such as doublet transitions at about 130 , 90 , and 20°C . The mean value of the two transition temperatures in absolute scale, 245°K . (-28°C .), is nearly equal to two-thirds of the first-order transition temperature at about 363°K . (90°C .).

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Résumé

On a mesuré la relaxation de la tension de compression, l'expansion linéaire thermique et des propriétés diélectriques du polytétrafluoroéthylène (PTFE) dans une gamme de températures comprises entre -60 et 10°C . Lors de la mesure de la tension de relaxation entre -55 et 5°C avec des intervalles de 5°C , on a obtenu une courbe maîtresse qui se superpose bien avec une série de courbes de tension de relaxation provenant des mêmes spécimens à différentes températures et cela en appliquant la méthode dite de réduction de Ferry. On a porté graphiquement la valeur logarithmique du facteur de réduction a_T à différentes températures en fonction de l'inverse de la température absolue et on a aussi obtenu un diagramme de l'énergie d'activation apparente en fonction de la température au départ de la pente de la courbe $\log a_T$ en fonction de $1/T$. Il existe deux maxima très bien caractérisés à environ -40 et -15°C dans le diagramme de l'énergie d'activation apparente. Les valeurs des modules de relaxation à la compression mesurées à un temps déterminé après la compression ont été portées graphiquement en fonction de la température et la courbe offre deux illustrations remarquable de la variation du module de Young à environ -40 et -15°C . Sur la courbe du coefficient d'expansion linéaire thermique en fonction de la température, on a observé deux plateaux à environ -40 et -15°C pour divers spécimens de PTFE de cristallinité variable. La valeur de $T_g \frac{3(\alpha_1 - \alpha_2)}{A}$ était d'environ 0.04 où T_g est la valeur moyenne des deux températures de transition en ($^{\circ}\text{K}$), α_1 , et α_2 sont des coefficients d'expansion linéaire thermique au dessus et en dessous des deux transitions et A est la fraction amorphe de chaque échantillon. La mise en graphique de chaque tangente des pertes diélectriques, $\tan \delta$, et de la constante diélectrique ϵ' mesurée à l'aide d'un pont de Schering à une fréquence de 50 cycles/sec en fonction de la température, a fourni deux dispersions de $\tan \delta$ à environ -35 et -25°C et deux variations irrégulières de ϵ' dans la même région de températures. Sur la base de ces mesures, on a conclu que les deux transitions de second ordre ont lieu dans le PTFE à environ -40 et -15°C . La valeur moyenne des deux températures de transition en échelle absolue, 245°K (-28°C) égale environ les deux tiers de la température de transition du premier ordre à environ 363°K (90°C).

Zusammenfassung

Messungen der Kompressionsspannungsrelaxation, der linearen thermischen Ausdehnung und der dielektrischen Eigenschaften wurden an gepresstem Polytetrafluoräthylen (PTFE) im Temperaturbereich -60 – 10°C ausgeführt. Bei der Messung der Spannungsrelaxation im Bereich -55 – 5°C in 5°C -Intervallen wurde eine Masterkurve erhalten, welche für eine Reihe von Spannungsrelaxationskurven für die gleiche Probe bei verschiedenen Temperaturen bei Anwendung der sogenannten Reduktionsmethode nach Ferry gute Übereinstimmung zeigte. Der Reduktionsfaktor a_T bei verschiedenen Temperaturen wurde im logarithmischen Netz gegen den Reziprokwert der absoluten

Temperatur aufgetragen und aus der Neigung der $\log a_T$ gegen $1/T$ -Kurve ein Diagramm der scheinbaren Aktivierungsenergie gegen die Temperatur erhalten. Im Diagramm der scheinbaren Aktivierungsenergie traten zwei scharfe Maxima bei etwa -40 und -50°C auf. Die Kompressionsrelaxationsmoduln bei einer bestimmten Zeit nach der Kompression wurden gegen die Temperatur aufgetragen und an der Kurve bemerkenswerte Änderungen des Young-Moduls bei etwa -40 und -15°C festgestellt. Auf der Kurve für den linearen thermischen Ausdehnungskoeffizienten gegen die Temperatur wurde für einige PTFE-Proben mit verschiedener Kristallinität bei etwa -40 und -15°C zwei Stufen beobachtet. Der Wert von $T_g \frac{3(\alpha_1 - \alpha_3)}{A}$ betrug etwa 0.04 ; hier ist T_g der Mittelwert der beiden Umwandlungstemperaturen ($^\circ\text{K}$), α_1 und α_3 sind die linearen thermischen Ausdehnungskoeffizienten oberhalb und unterhalb der beiden Umwandlungen und A ist der amorphe Anteil jeder Probe. Das Diagramm des mit einer Scheringbrücke bei einer Frequenz von 50 hz gemessenen dielektrischen Verlusttangens $\tan \delta$ und der Dielektrizitätskonstanten ϵ' gegen die Temperatur lieferte zwei Dispersionsgebiete für $\tan \delta$ bei etwa -35 und -25°C sowie zwei irreguläre Änderungen von ϵ' in den gleichen Temperaturbereichen. Diese Messungen führen zu dem Schluss, dass in PTFE bei etwa -40 und -15°C zwei Umwandlungen zweiter Ordnung auftreten. Der Mittelwert der beiden Umwandlungstemperaturen beträgt 245°K (-28°C) und ist nahezu gleich $2/3$ der Umwandlungstemperatur erster Ordnung bei etwa 363°K (90°C).

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