

Thermal Expansion of Irradiated Polytetrafluoroethylene

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Synopsis

The thermal expansion coefficient of gamma-irradiated Polytetrafluoroethylene (PTFE) has been measured in the temperature range 80–340 K by using a three-terminal capacitance technique. The samples are irradiated in air at room temperature with gamma rays from a Co^{60} source at a dose rate of 0.26 Mrad/h. The change in crystallinity is measured by an x-ray technique. The expansion coefficient is found to increase with radiation dose below 140 K owing to the predominant effect of degradation. Above 140 K, the expansion coefficient is found to decrease with radiation dose because of the enhanced crystallinity. The temperatures of the two first-order phase transitions are also found to shift to lower temperatures owing to degradation of PTFE.

INTRODUCTION

Information about the thermal properties of irradiated polymers is useful both from the scientific and the technological point of view. Although there have been a few studies on the specific heat and thermal conductivity of irradiated polymers, no studies have been reported on their thermal expansion.¹ We have undertaken the investigation of the thermal expansion of a few technologically important polymers like poly(methyl methacrylate) polystyrene, polytetrafluoroethylene, and polyoxymethylene as a function of radiation dose at low temperatures. This paper presents our results of thermal expansion studies on irradiated polytetrafluoroethylene (PTFE) in the temperature range 80–340 K.

PTFE is a partially crystalline polymer whose radiation chemistry has been reviewed extensively in the literature.^{2–4} PTFE has been found to undergo main-chain degradation under irradiation. This fact has been confirmed by molecular weight measurements,^{5,6} mechanical strength measurements,^{7–12} tensile creep measurements,¹³ and IR spectroscopy.¹⁴ The crystallinity of PTFE has also been found to increase with radiation dose at low and moderate dosages and to decrease at very high dosages. This has been found by specific volume measurements,¹⁵ density measurements,^{14–17} dynamic mechanical studies,¹⁷ IR studies,¹⁴ DSC studies,¹⁸ electron microscopy,¹⁹ and x-ray diffraction studies.^{20,21} PTFE exhibits two first-order phase transitions near 19 and 30°C, which have been found to shift to lower temperatures due to irradiation.^{14,15,19,22,23} Although there has been no study about the thermal expansion and specific heat of irradiated PTFE, its thermal conductivity has been studied.^{22,24}

EXPERIMENTAL

Irradiation Procedure

Commercial grade PTFE (Teflon) is used in the present investigation. Samples of length and diameter, each 1 cm, cut from a Teflon rod were irradiated in air at room temperature with gamma rays from a Co^{60} source at a dose rate of 0.26 Mrad/h. The samples were irradiated to various integral dosages; 10, 30, 50, 100, 200, 300, 400, and 500 Mrad.

Crystallinity Measurements

The crystallinity changes induced by irradiation were found by x-ray crystallography by using a Philips Model PW-1050/70 diffractometer and nickel-filtered CuK_α radiation. The x-ray diffraction pattern taken for the powdered samples irradiated to various dosages are shown in Figure 1. PTFE gives a well-defined crystalline peak at an angle of $2\theta = 18^\circ$. The ratio of the

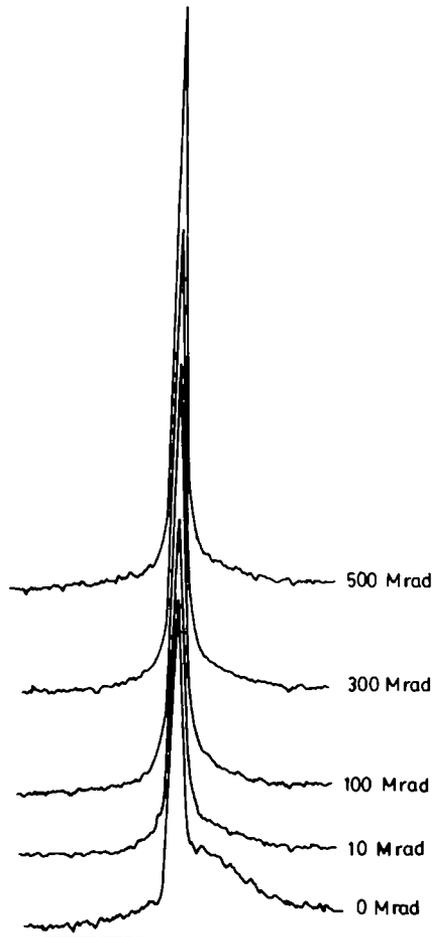


Fig. 1. X-ray diffraction pattern.

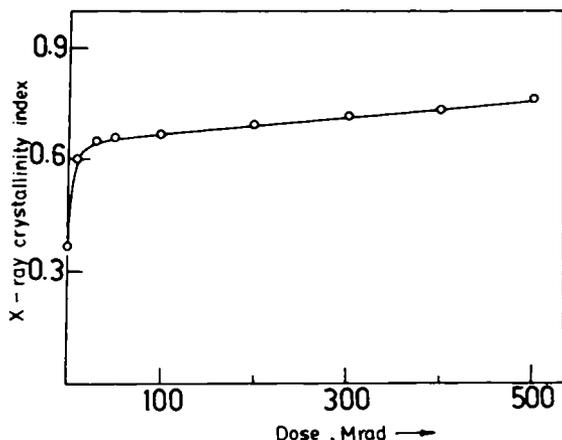


Fig. 2. Variation of crystallinity with radiation dose.

areas of crystalline scattering peak to the total scattering area (crystalline plus amorphous scattering) is taken as an index of crystallinity. The variation of the x-ray crystallinity index as a function of radiation dose is shown in Figure 2. The index is found to increase from 0.36 at 0 Mrad to 0.76 at 500 Mrad. The increase is rapid in the range 0–10 Mrad, less rapid in the range 10–50 Mrad, and finally becomes linear between 50 and 500 Mrad. The increase in crystallinity is the result of chain scission occurring preferentially in the amorphous regions, leading to strain relaxation and the formation of additional crystalline regions. Although other workers report that the x-ray crystallinity increases at low dosages but decreases at high dosages, our measurements do not show decrease at high dosages. This may be due to the low initial crystallinity of our samples, whereas the samples used by other workers had very high initial crystallinity.

Thermal Expansion Apparatus

The thermal expansion coefficients of samples are measured by the three-terminal capacitance technique, which has been described in detail elsewhere.²⁵ In this technique the changes in the length of the sample are converted into changes in electrical capacitance, which is then measured by using a ratio transformer bridge to a resolution of one part per million.²⁶

The temperature of the sample was measured by a platinum resistance thermometer and controlled to a resolution of 0.1 K by a Lake Shore Cryotronics digital thermometer/controller Model DRC-84C.

Measuring Procedure

The two circular faces of the cylindrical samples were polished to render them flat and parallel. The sample was mounted in the capacitance cell and cooled to liquid-nitrogen temperature slowly over a period of 12 h. The sample was heated in steps of 6 K by using the temperature controller. Around the phase transition regions, the heating was done in steps of 1 K. For every stabilized temperature (stable over at least 45 min), as indicated by no

thermal gradients across the sample and the cell, the ratio transformer bridge was balanced and the reading taken, which gives $1/C$ directly. Thus the values of T and $1/C$ were recorded in the temperature range 80–350 K for PTFE samples irradiated to 0, 10, 100, 300, and 500 Mrad. The thermal expansion coefficient was calculated using the equation

$$\alpha_s = \left(\frac{L_c}{L_s} \right) \alpha_c - \left(\frac{0.15625}{L_s} \right) \frac{d}{dT} (1/C)$$

where L_s is the length of the sample and L_c is the length of the cell that contributes to the differential expansion of the gap. α_c is the expansivity of the cell, which was determined by a calibration experiment by using aluminium and germanium as standard references and which has been described in detail elsewhere.²⁵ The derivative $(d/dT)(1/C)$ is approximated by the numerical derivative $\Delta(1/c)/\Delta T$ at the average temperature between any two adjacent readings. The accuracy in the measurement of α is about 4%. The relative expansion of the sample was calculated from the formula,

$$\left(\frac{\Delta l}{l} \right)_s = \frac{L_c}{L_s} \left(\frac{\Delta l}{l} \right)_c - \left(\frac{0.15625}{L_s} \right) \Delta(1/C) \quad (2)$$

RESULTS AND DISCUSSION

Thermal expansion coefficients for the PTFE samples irradiated to various dosages are plotted together in Figure 3 as a function of temperature. The

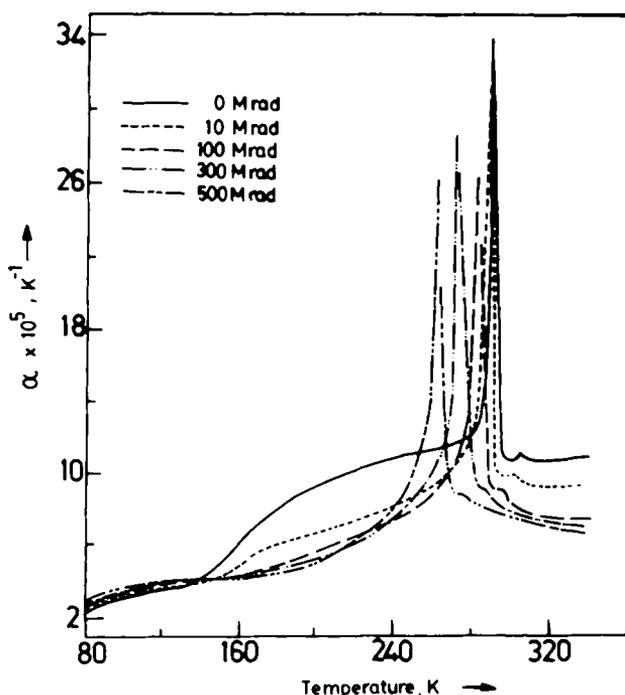


Fig. 3. Variation of α with temperature.

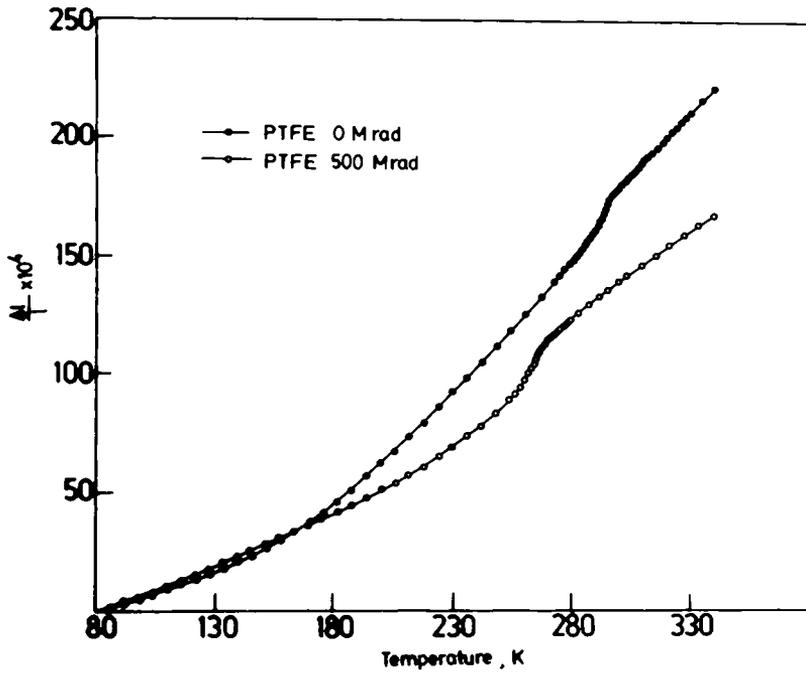


Fig. 4. Variation of $\Delta l/l$ with temperature.

variation of the relative expansion for samples irradiated to 0 and 500 Mrad as a function of temperature is shown in Figure 4. The variation of α with radiation dose at representative temperatures, 80, 190, and 310 K, are shown in Figure 5.

The temperature of the two first-order phase transitions are found to shift to lower temperatures with increasing radiation dose as shown in Figure 6.

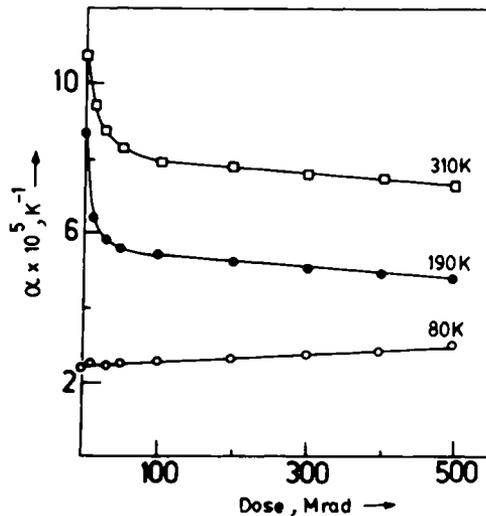


Fig. 5. Variation of α with radiation dose.

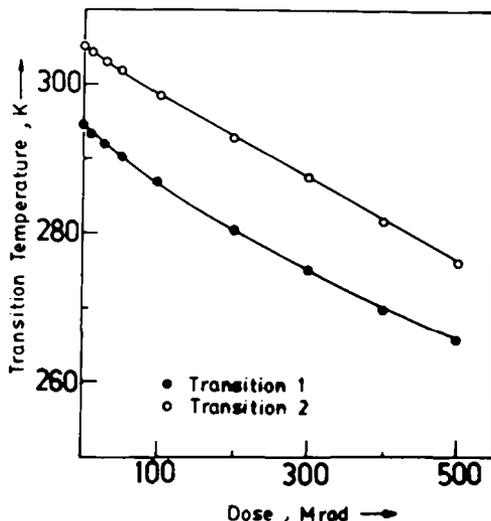


Fig. 6. Variation of transition temperature with radiation dose.

The temperatures of both transitions are found to shift by equal extents. The dependence of transition temperatures on radiation dose is very similar to that found by Kusy and Turner¹⁸ by DSC. The degradation of PTFE resulting in an overall reduction in chain length caused by irradiation is responsible for the observed shift in both transition temperatures.²⁷ The gamma relaxation around 160 K for the unirradiated sample is also found for the sample irradiated to 10 Mrad at about the same temperature but is less pronounced. For the samples irradiated to higher dosages from 100 to 500 Mrad, this relaxation is not observed. This may be due to the high crystallinity at higher dosages and the dominant first-order transition that shifts to lower temperatures at higher dosages.

From Figure 3 it is seen that the thermal expansion coefficient α increases with radiation dose in the temperature range 80–140 K. In the range 140–160 K this behavior reverses the trend and shows a decrease with radiation dose. This behavior is shown in Figure 5 for the dose dependence of α at 190 K. At this temperature α decreases very rapidly with dose up to 10 Mrad, thereafter less rapidly up to about 100 Mrad, and afterwards decreases linearly with dose. The same trend also persists at higher temperatures beyond the phase transition.

The increase in α with radiation dose between 80 and 140 K is due to radiation-induced degradation of PTFE. During every scission of the main polymer chain, a covalent bond is broken. The two stable end groups formed at the scission point will exhibit van der Waals interactions. The thermal expansion coefficient, being dependent on the strength of interaction of constituent units, is larger for a solid with van der Waals interactions than for a solid that is covalently bonded. This conclusion is supported by thermal expansion studies on oriented crystalline polymers. As the draw ratio is increased, the polymer chains become aligned along the draw direction; as a result the thermal expansion coefficient α perpendicular to the draw direction increases owing to the relative increase in the interchain van der Waals

interactions. Furthermore, the thermal expansion coefficient of oriented PTFE shows that, below T_g , α increases with increasing draw ratio, whereas above T_g it first decreases, passes through a minimum, and then increases.²⁸

The decrease in α above 140 K with radiation dose is due to increased crystallinity. The effect of crystallinity on thermal expansion is predominant only above the glass transition temperature.^{29,30} Since the expansion coefficient of a glass is only slightly greater than that of the corresponding crystalline polymer below T_g , where the amorphous regions are in the glassy state, expansivity is independent of crystallinity. But above T_g , a large increase in expansivity with decreasing crystallinity is expected, since the expansion coefficient for a liquid or rubbery phase is much larger than that of the corresponding crystalline phase. The sharp decrease in α at 190 K and at 310 K at lower dosages and a slow decrease at higher dosages correspond to a similar opposite trend observed in the dose dependence of crystallinity shown in Figure 5. Similar results have been obtained by Araki et al.,³¹ who found that α of PTFE decreases with increasing crystallinity in the region above the room-temperature transition. The heat capacity measurements of Lau et al.³² also show similar behavior.

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