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Effect of X-ray irradiation on the thermal expansion of polymers

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The coefficient of linear thermal expansion (α) of ordinary (non-X-ray irradiated) and X-ray irradiated samples of polyester, glass-fibre reinforced polyethylene and polytetrafluoroethylene, has been determined in the temperature range 30 to 200° C using a two-terminal capacitance technique. The temperature corresponding to the sudden increase in α of the X-ray irradiated samples are higher than those corresponding to the ordinary samples. The values of α for X-ray irradiated samples are smaller than those of ordinary samples for polyester and glass-fibre reinforced polyethylene over the entire temperature range of this study. For polytetrafluoroethylene the values of α of the X-ray irradiated sample are lower than those corresponding to the ordinary samples at lower temperatures, and this trend is reversed at higher temperatures. The results are explained in the light of the change in the polymer structure brought about by X-ray irradiation.

1. Introduction

Polymers are extensively used today in place of metals and other engineering materials. The application of the polymers will be highly enhanced through a thorough knowledge of their physical properties apart from the chemical properties. The various physical properties, such as thermal expansion [1–7], thermal and electrical conductivities [8–14], heat capacity [15–17] and acoustic properties of the polymers [18–20] have been extensively studied. These studies have been found to be highly useful in understanding the relaxation behaviour of the polymers. Radiation damage also influences the structure of the polymers and hence their physical properties. Studies of the effect of irradiation on electrical conductivity of polymers [21–23] indicate an enhancement of conductivity owing to changes brought about in the polymer structure due to radiation effects. Studies of the effect of irradiation on the thermal expansion of polymers are scanty. In view of this, an attempt is made to study the effect of X-ray irradiation on the thermal expansion of polyester, glass-fibre reinforced polyethylene and polytetrafluoroethylene, and the results are reported in this paper.

2. Experimental details

The linear thermal expansion coefficient of the polymers has been determined by measuring the change in the length of the specimen as a function of temperature using a two-terminal capacitance technique. The design of the mechanical apparatus is similar to the arrangement developed by Rao and Jayasri Maiti [24] with a few modifications. In this technique the changes in the length of the specimen at different temperatures are magnified ten times using a mechanical lever arrangement. The specimen is in the form of a cylindrical bar, about 0.017 m long and about 0.004 m diameter. It is mounted inside a specially made tubular heater of suitable size on a rigid asbestos base which is kept inside the heater at the bottom. A thin tapered fused quartz rod, 0.05 m long, and having a diameter of 0.005 m, is mounted on top of the specimen. The pointed end of the fused quartz rod will be in contact with a thin duraluminium rod, 0.3 m long. A fulcrum arrangement is used to divide the length of the aluminium rod in the ratio of 1:10. This forms the mechanical lever. The sample arrangement is on the smaller length side of the aluminium rod from the fulcrum. At the other end of the lever is attached a brass plate forming one of the plates of the parallel plate condenser, the other plate of the condenser being on an iron cylindrical block with parallel end surfaces. The changes in the length of the specimen result in corresponding changes in the air gap of the parallel plate condenser and hence are registered as changes in the capacitance of the parallel plate condenser. Since this capacitor forms a part of the tuned circuit of the Clapp oscillator shown in Fig. 1, changes in the capacitance lead to corresponding changes in the resonant frequency of the oscillator.

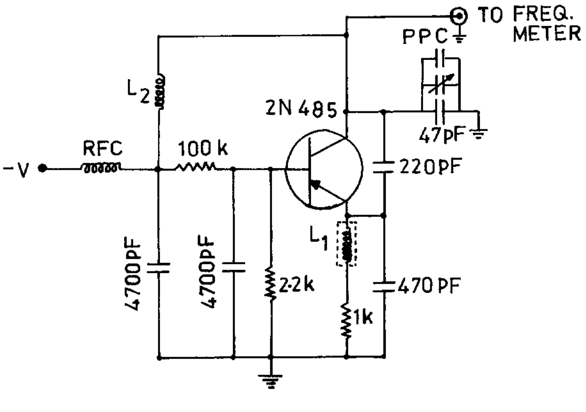

Figure 1 Electronic apparatus of the Clapp oscillator.

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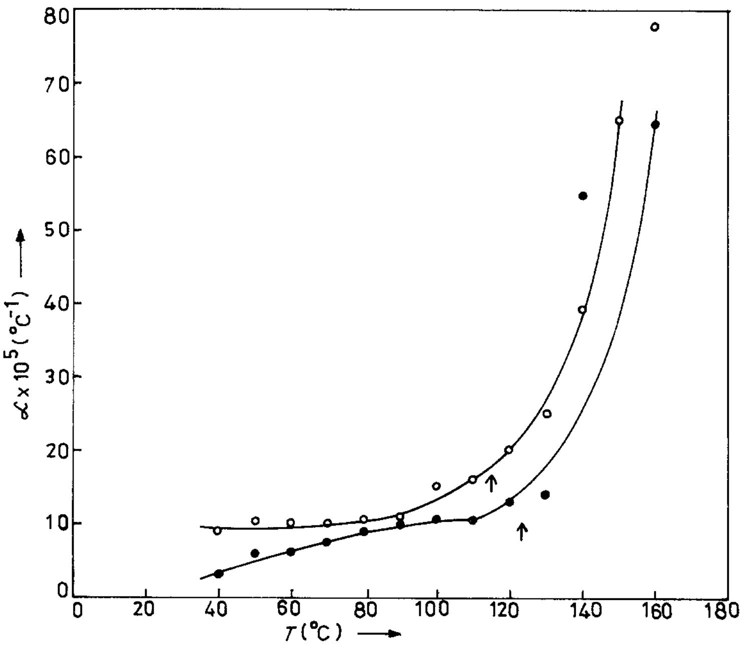


Figure 2 Variation of α with temperature for polyester. (○) Ordinary, (●) X-ray irradiated.

Hence the change in the length of the specimen (Δl) can be related to the change in the frequency (Δf) of the oscillator by the following equation [25]

$$\Delta l = \frac{A}{10(4\pi C^2)}\left(\frac{\partial C}{\partial f}\right)\Delta f \qquad (1)$$

where A is the area and C the capacitance of the parallel plate condenser. Substituting the value of $A = 19.64 \times 10^{-4}\,\text{m}^2$ and using any necessary conversion factors we obtain

$$\Delta l = 1.38 \times 10^{-4}\frac{1}{C^2}\left(\frac{\partial C}{\partial f}\right)\Delta f\text{m} \qquad (2)$$

Using typical values corresponding to the present case such as $C = 4.06\,\text{pF}$, $\partial C/\partial f = 0.2134\,\text{pF (kHz)}^{-1}$ and $l = 0.02\,\text{m}$ we obtain

$$\frac{\Delta l}{l} = 0.89 \times 10^{-7}\Delta f \qquad (3)$$

Since the frequency of the oscillator can be measured correct to 10 Hz using a Yamuna Digital Frequency Counter Model no. 626, the accuracy of the present measurement of $\Delta l/l$ is of the order of 1 in 10^6.

3. Materials and methods

The polymer samples (polyester, glass-fibre reinforced polyethylene and polytetrafluoroethylene) were cut into bars of square cross-section from the bulk samples and then shaped into cylindrical specimens by grinding them in a split cylindrical die using fine carborundum powder with a little water as abrasive. The cross-sections of the cylindrical rods were fairly uniform throughout their lengths and the end faces were perfectly flattened to be parallel to each other. The lengths of the samples at room temperature were measured using a comparator with an accuracy of $\pm 1 \times 10^{-6}\,\text{m}$. The densities of the samples were measured by the hydrostatic method. The lengths and densities of polyester, glass-fibre reinforced polyethylene and polytetrafluoroethylene were 1.6673×10^{-2}, 1.6678×10^{-2} and $1.6190 \times 10^{-2}\,\text{m}$, and 1.260, 1.545 and $2.068\,\text{Mg}\,\text{m}^{-3}$, respectively.

To study the effect of X-ray irradiation on the thermal expansion of polymers, X-ray irradiation was effected on the polymer samples by mounting them in the direction of the X-rays coming from the window of the X-ray tube. The target of the X-ray tube was copper. It was operated at 30 kV, 10 mA. A collimated beam of 1 mm diameter was allowed to pass through the cylindrical polymer sample along the axis of the cylinder. The diameters of the cylindrical samples of polyester, glass-fibre reinforced polyethylene and polytetrafluoroethylene were 4.05, 4.10 and 4.04 mm, respectively. All the polymer samples studied in this work were irradiated with X-rays for 1 h. The samples were used immediately after irradiation for the thermal expansion measurement.

A specially designed tubular furnace was used to raise the temperature of the specimen. The specimen was usually set at the centre of the furnace. The specimen temperature was maintained at any desired value to within $\pm 0.2°$C using the APLAB temperature controller with indicator, model no. 9601. The sensor was an iron–constantan thermocouple, and was kept very close to the mid-point of the specimen, while the axis of the cylindrical specimen coincided with the axis of the tubular furnace. The temperature of the furnace could be varied by regulating the current through the cylindrical heater. In the present study, the expansion of the fused quartz rod, placed above the sample inside the furnace, was neglected in comparison with the expansion of the sample (polymers have high thermal expansion coefficient) since the linear thermal expansion coefficient of fused quartz was $0.5 \times 10^{-6}\,°\text{C}^{-1}$.

4. Results and discussion

The change in the length of polyester, glass-fibre reinforced polyethylene and polytetrafluoroethylene, both ordinary (non-X-ray irradiated) and X-ray irradiated samples, as a function of temperature was determined by measuring the change in the frequency of the oscillator and making use of Equation 2. The linear thermal expansion coefficients of the polymers at

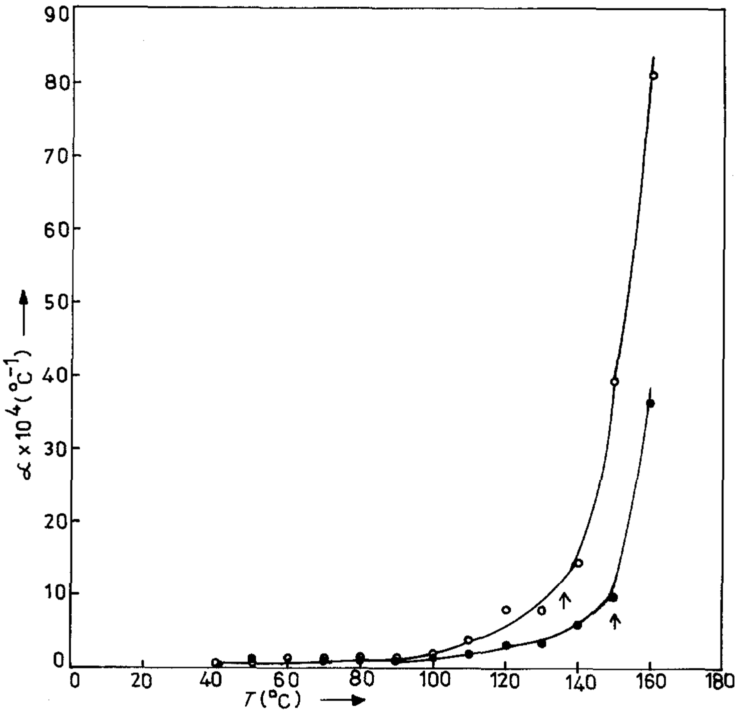


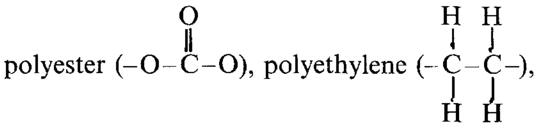
Figure 3 Variation of α with temperature for glass-fibre reinforced polyethylene. (○) Ordinary, (●) X-ray irradiated.

different temperatures, both for ordinary and X-ray irradiated samples, were evaluated using the relation

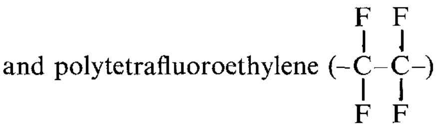
$$\alpha = \frac{1}{l_T}\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_T \tag{4}$$

where l_T represents the length of the sample at temperature T. dl represents the elemental change in length l_T due to an elemental change in T by dT. $(\mathrm{d}l/\mathrm{d}T)_T$ has been evaluated using the curves Δl against T. The data of α against T for both ordinary and X-ray irradiated polymers are given in Tables I to III. The variation of α with temperature for these polymers is shown in Figs 2 to 4.

An examination of the data presented in Figs 2 to 4 indicates that α increases with increase in temperature both for ordinary and X-ray irradiated samples. The values of α for X-ray irradiated samples are smaller than those of ordinary samples for polyester and glass-fibre reinforced polyethylene. For polytetrafluoroethylene, the values of α of X-ray irradiated samples at low temperatures are higher than those corresponding to ordinary samples, and at higher temperatures the trend is reversed. These observations indicate clearly the effect of X-ray irradiation on the polymer structure. The characteristic chain group of the polymers:



polyester $(\mathrm{-O-\overset{\overset{\large O}{\|}}{C}-O})$, polyethylene $(\mathrm{-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-})$,



and polytetrafluoroethylene $(\mathrm{-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-})$

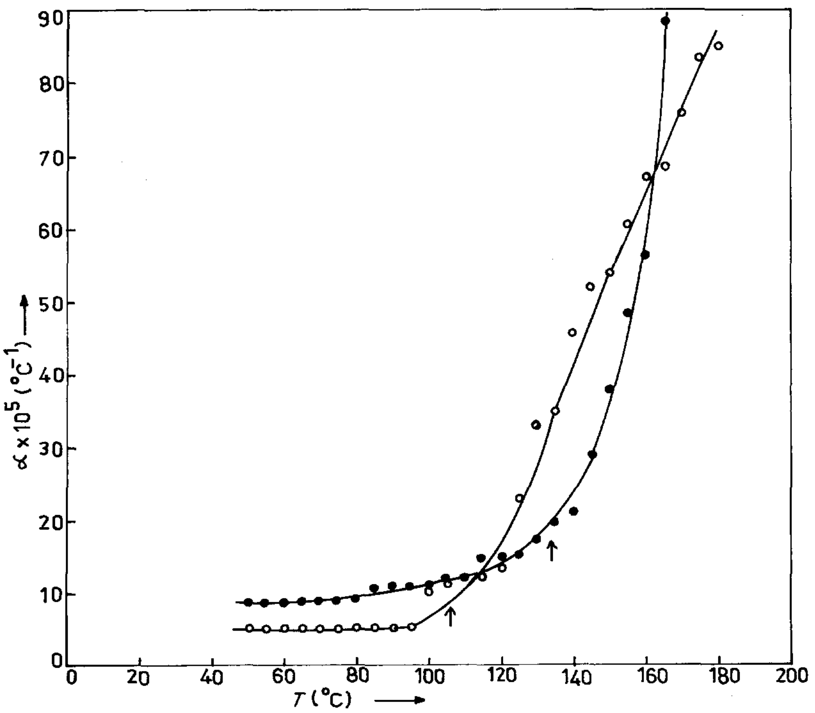


Figure 4 Variation of α with temperature for polytetrafluoroethylene. (○) Ordinary, (●) X-ray irradiated.

TABLE I Variation of linear thermal expansion coefficient with temperature for polyester

Temperature (° C)	$\alpha \times 10^5$ (° C^{-1})	
	Ordinary sample	X-ray irradiated sample
40	9.2	3.0
50	10.0	6.0
60	10.0	6.0
70	10.0	7.6
80	10.4	9.3
90	10.9	10.2
100	14.9	10.6
110	16.2	10.7
120	19.8	13.2
130	24.7	19.3
140	39.3	55.3
150	65.2	82.6
160	77.5	64.5

TABLE II Variation of linear thermal expansion coefficient with temperature for glass-fibre reinforced polyethylene

Temperature (° C)	$\alpha \times 10^5$ (° C^{-1})	
	Ordinary sample	X-ray irradiated sample
40	7.0	4.2
50	7.0	8.4
60	13.3	8.7
70	13.3	6.3
80	14.9	7.4
90	15.9	12.7
100	21.0	17.9
110	37.1	23.8
120	78.6	32.7
130	78.2	35.5
140	144.9	61.8
150	395.5	102.9
160	814.0	367.6

TABLE III Variation of linear thermal expansion coefficient with temperature for polytetrafluoroethylene

Temperature (° C)	$\alpha \times 10^5$ (° C^{-1})	
	Ordinary sample	X-ray irradiated sample
50	4.7	8.5
55	4.7	8.9
60	4.7	8.9
65	4.7	9.2
70	4.7	9.2
75	4.7	9.2
80	4.7	9.2
85	4.7	10.9
90	4.7	10.9
95	4.7	10.9
100	10.2	10.9
105	11.1	12.3
110	12.3	12.3
115	12.3	14.7
120	13.6	15.0
125	22.9	15.3
130	33.3	17.5
135	34.8	20.3
140	45.7	21.3
145	52.1	29.2
150	53.9	37.9
155	60.5	48.6
160	67.0	56.5
165	68.5	88.5

TABLE IV Temperature corresponding to sudden rise in α, $T_{\alpha,\mathrm{R}}$, for polymers

Polymer	$T_{\alpha,\mathrm{R}}$ (° C)	
	Ordinary sample	X-ray irradiated sample
Polyester	115	123
Glass-fibre reinforced polyethylene	136	151
Polytetrafluoroethylene	106 (127)*	134

*[27].

may become affected by X-ray irradiation, leading to changes in the linear thermal expansion coefficient. Since the polymer structure is also sensitive to temperature, the present study of the effects of X-ray irradiation on α indicates the breakdown of the polymer structure due to irradiation. It is worthwhile to note here that an enormous increase in conductivity of polyethylene [26] was observed when irradiated with high-energy gamma-radiation which indicates the change in polymer structure. A change in polymer behaviour from insulating to conducting occurs. The lower values of α for the polymers after X-ray irradiation observed in the present study indicate a hardening of the polymer owing to the breakdown of the polymer chain structure, an aspect which needs further investigation. To gain more insight into the effect of radiation on polymer structure and properties, it would be worthwhile to study the effect of X-ray irradiation time and dosage intensity, gamma-ray irradiation and ultraviolet irradiation, and work along these lines is in progress.

From Figs 2 to 4, it is clear that α of the polymers increases suddenly at a particular temperature – the glass transition temperature. The temperature at which α increases suddenly, ($T_{\alpha,\mathrm{R}}$), is indicated in the figures by arrows and the values are listed in Table IV. The $T_{\alpha,\mathrm{R}}$ values corresponding to X-ray irradiated samples are higher than those corresponding to ordinary samples indicating clearly the influence of X-ray irradiation on polymer structure and hence on their physical properties.

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