Thermal expansion of irradiated poly(methyl methacrylate)

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The thermal expansion coefficient of irradiated poly(methyl methacrylate) is measured in the temperature range 80–350 K using a three-terminal capacitance technique. The samples are irradiated with gamma-rays from a ^{60}Co source in air at room temperature. The infra-red spectra are taken to indicate radiation-induced changes. The thermal expansion coefficient of poly(methyl methacrylate) is found to increase with radiation dose, the increase being larger at higher temperatures. This has been explained as due to the relative increase in the van der Waals interaction caused by radiation-induced degradation.

(Keywords: thermal expansion; low temperature; radiation effects; poly(methyl methacrylate))

INTRODUCTION

Information about the thermal properties of irradiated polymers is useful from both scientific and technological points of view. While 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 an investigation of the thermal expansion of a few technically 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 poly(methyl methacrylate) (PMMA) in the temperature range 80–350 K.

The effect of irradiation on PMMA has been extensively reviewed in the literature[2–4]. PMMA primarily undergoes degradation under the influence of radiation. This has been confirmed by intrinsic viscosity measurements[5–8], the g.p.c. technique[9] and the light scattering method[6]. It has been established that PMMA undergoes only main-chain scission without any simultaneous crosslinking under irradiation[6]. Main-chain scission is found to occur at random since the ratio $\bar{M}_w/\bar{M}_n$ determined as a function of dosage is found to approach a value of 2 at higher dosages[10,11], in accordance with the theoretical prediction[12]. Oxygen has been found to exert a protecting effect on the radiation degradation of PMMA[7]. This effect is found to be more prominent when the sample is in the form of finely divided powder than as bulk[13,14]. Many additives have been found to reduce the radiation degradation yield in PMMA significantly[14–18]. On the other hand, it has also been found that commercial PMMA sheets containing a plasticizer degrade faster than unplasticized PMMA[19]. While there have been a few attempts to elucidate the thermal conductivity of irradiated PMMA, no measurements have been reported on the specific heat and thermal expansion.

EXPERIMENTAL

Irradiation procedure

Commercial-grade PMMA ('Perspex') was used for our investigations. Samples of length ~1 cm and diameter 1 cm cut from a Perspex rod were irradiated in air with gamma-rays from a ^{60}Co source at a rate of 0.26 Mrad h^{-1} at room temperature. The irradiation was performed in the gamma chamber at the Cotton Technological Research Laboratory, Bombay, to various dosages from zero to 50 Mrad, in steps of 10 Mrad, and from 100 to 500 Mrad, in steps of 100 Mrad. The colourless transparent samples turned yellow at lower dosages (<100 Mrad) and turned brown at higher dosages (>100 Mrad). This colouring of the sample has also been observed by other workers[13,20]. Above 50 Mrad, bubbles appeared inside the sample due to the evolution of gases, and as a consequence the sample developed cracks, became brittle and was unsuitable for thermal expansion measurements.

Infra-red spectra

The infra-red spectrum of the unirradiated and irradiated samples in powder form with mujol are recorded with a Schimatzu i.r. spectrophotometer. The spectra for the unirradiated sample and that irradiated to 50 Mrad are shown together in *Figure 1*, to facilitate comparison. The 1720 cm^{-1} band arising from C=O stretching[21] is increased in intensity due to irradiation. The two doublets at 1140 and 1200 cm^{-1} and at 1240 and 1255 cm^{-1}, arising from C–O–C stretching[22], also show an increase in intensity. Similarly, the intensities of the absorption bands at 980 cm^{-1} due to O–CH$_3$ rocking, at 840 cm^{-1} due to CH$_2$ rocking and at 750 cm^{-1} due to C–C skeletal vibration[23] also show increases. This seems to be due to radiation-induced degradation, because of which various modes of vibration can occur relatively more freely because of the formation of shorter polymer chains.

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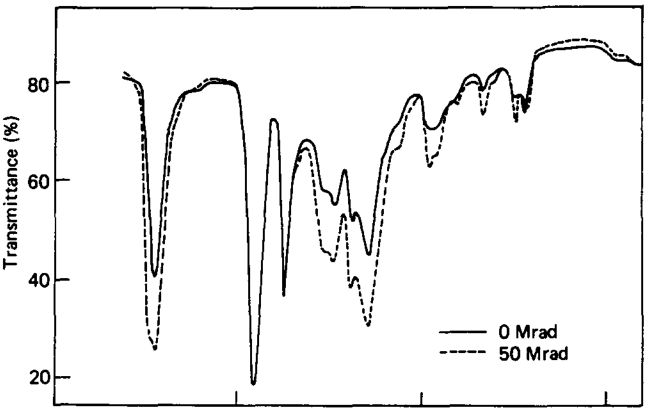

Figure 1 I.r. spectrum

Thermal expansion apparatus

The thermal expansion coefficient of the samples are measured by using the three-terminal capacitance technique, which has been described in detail elsewhere[24]. In this technique, 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[25,26].

Temperature of the sample is measured by a platinum resistance thermometer and controlled to a resolution of 0.1 K by using a Lake Shore Cryotronics digital thermometer/controller model DRC-84C.

Measuring procedure

The two circular ends of the cylindrical PMMA samples are polished to render them flat and parallel to each other. The sample is mounted in the capacitance cell and cooled to liquid-nitrogen temperature slowly over a period of 12 h. The sample is heated in steps of 6–8 K by using the temperature controller. For every stabilized temperature, stable over at least 45 min, as indicated by the absence of gradients across the sample and the cell, the ratio transformer reading is taken, which gives $1/C$ directly. Thus the value of $1/C$ *versus* T is recorded in the temperature range 80–340 K for PMMA samples irradiated to various dosages like 0, 10, 20, 30, 40 and 50 Mrad.

The thermal expansion coefficient is calculated from:

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

Here L_s is the length of the sample and L_c is the length of the cell that contributes to the differential expansion. L_c is given by the sum of L_s and the capacitor gap. The factor 0.15625 is an instrumental constant determined from the dimensions of the capacitor plate. The expansivity of the cell, α_c, is determined using aluminium and germanium as standard references, as described elsewhere[24]. The derivative $d(1/C)/dT$ is determined by fitting the data of $1/C$ *versus* T into a cubic spline with two equispaced knots and then differentiating. *Figure 2* shows the variation of thermal expansion coefficient of PMMA samples irradiated to 0, 10, 30 and 50 Mrad dosage in the temperature range 80–340 K. The accuracy in the measurement of α_s is about 4%. The relative expansion $(\Delta l/l)$ of the samples is calculated from:

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

Figure 3 shows $(\Delta l/l)$ calculated for PMMA samples irradiated to 0 and 50 Mrad in the temperature range 80–340 K. *Figure 4* shows the variation of α of PMMA as a function of radiation dosage for a few representative temperatures.

RESULTS AND DISCUSSION

Figures 2 and *4* show that α of PMMA increases with radiation dose at all temperatures. However, the increase in α is larger at high temperature. For a dose of 50 Mrad, the increase in α is about 15% at 330 K, 12.5% at 300 K and 6% at 220 K. Further, the increase in α is rapid at lower dosages, i.e. in between 0 and 10 Mrad, and thereafter becomes steady at all temperatures. For example, at 330 K, the dose rate of increase in α is $0.06 \times 10^{-5}\ K^{-1}\ Mrad^{-1}$ in between 0 and 10 Mrad, whereas it is $0.01 \times 10^{-5}\ K^{-1}\ Mrad^{-1}$ in between 10 and 50 Mrad. At 220 K, these values are $0.015 \times 10^{-5}\ K^{-1}\ Mrad^{-1}$ and $0.004 \times 10^{-5}\ K^{-1}\ Mrad^{-1}$ respectively.

The increase in α with radiation dose is due to main-chain degradation caused by radiation in PMMA. During every scission, a covalent bond in a polymer chain is broken. The two stable end groups that are formed at the scission point will have van der Waals interaction. The thermal expansion coefficient of a solid depends on the strength of interaction of constituent units. It is about two orders of magnitude greater for a solid whose molecules are held by van der Waals forces than for a covalently

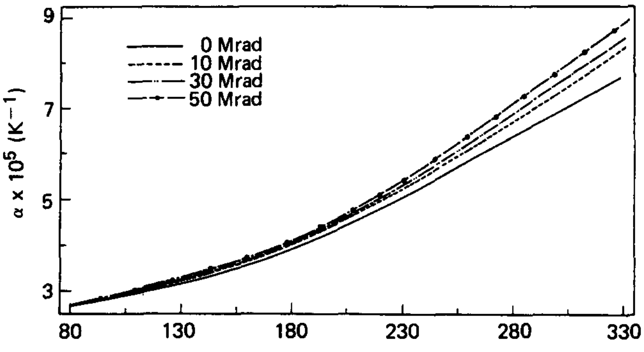

Figure 2 Variation of α with temperature

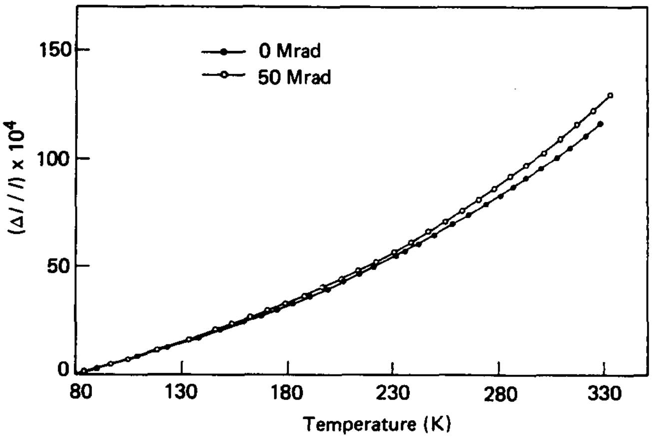

Figure 3 Variation of $\Delta l/l$ with temperature

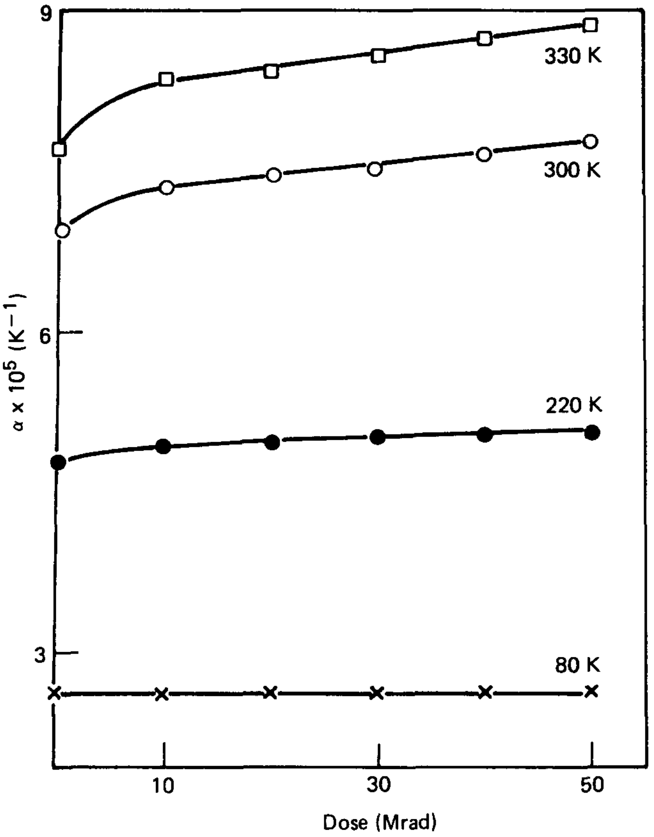

Figure 4 Variation of α with radiation dose

bonded solid. Thus, the relative increase in van der Waals bonds caused by the scission of the polymer chains by irradiation is responsible for the increase in α with radiation dose.

This conclusion is corroborated by similar results obtained during the study of the thermal expansion of oriented polymers[27]. As the draw ratio is increased from 2.57 to 3.75 in PMMA, the expansivity in the draw direction, α , decreases by 27% while the expansivity in a perpendicular direction, $\alpha_{\perp}$, increases by 8.4%. As the draw ratio is increased, the polymer chains become aligned along the draw direction so that the relative increase in the interchain van der Waals interaction causes an increase in $\alpha_{\perp}$. Radiation-induced scission plays a similar role in increasing expansivity.

The relative increase in van der Waals bonds caused by irradiation of PMMA has also been found to be responsible for the reduction in the thermal conductivity of irradiated PMMA[20].

The increase in thermal expansion coefficient with radiation dose has a temperature dependence, the increase in α being larger at higher temperature. This seems to arise from the temperature dependence of van der Waals interactions. The decrease in thermal conductivity due to irradiation of PMMA also has a similar temperature dependence[20]. The increase in α as a function of draw ratio in oriented amorphous polymers also shows a similar temperature dependence[27].

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