JOURNAL OF MATERIALS SCIENCE 28 (1993) 2423–2427

Thermal expansion of irradiated polypropylene from 10–340 K

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The coefficient of thermal expansion of gamma-irradiated polypropylene (PP) has been measured from 10–340 K by using the three-terminal capacitance technique. The samples were irradiated to 500 Mrad in air at room temperature with gamma rays from a ^{60}Co source at a dose rate of 0.26 Mrad h^{-1}. The crystallinity of the sample was measured by X-ray diffraction technique. The crystallinity was found to decrease with radiation dose from 55% at 0 Mrad to 44.7% at 500 Mrad. The thermal expansion coefficient was found to be almost constant with radiation dose from 10–125 K and decreases with radiation dose from 125–340 K.

1. Introduction

Information concerning the thermal properties of irradiated polymers is useful from both the scientific and technological points of view. Although there have been few studies on the specific heat and thermal conductivity of irradiated polymers, the thermal expansion of some of the technologically important polymers has been measured by Subrahmanyam and Subramanyam [1, 2].

Part of the interest in the radiation chemistry of polypropylene (PP) derives from its being intermediate in structure between polyethylene, which predominantly cross-links, and polyisobutylene, which only degrades. PP is known to exhibit characteristics of both cross-linking and degradation. While it has been reported that this polymer undergoes chain scission [3, 4] upon exposure to radiation, there have been other instances where it has exhibited cross-linking [5]. Dynamical mechanical property studies [6] and the work of Chappell *et al.* [7] indicate that high-energy irradiation of polypropylene produces cross-linking into a three-dimensional network accompanied by the destruction of crystallites and the loss of rigidity.

Polypropylene undergoes both cross-linking and degradation simultaneously during irradiation at low doses. The cross-linking slightly predominates over the chain scission. With increase in radiation dose, the rate of destruction caused by the radiation considerably increases. This leads to the formation of fragments of partially cross-linked molecules and low molecular fractions [8].

The radiation chemistry of PP has been extensively reviewed in the literature [9–12]. The thermal conductivity of irradiated PP at high doses and at high temperatures has been studied by Tomilson and Kline [13]. In the present paper, results on thermal expansion of irradiated polypropylene in the temperature range 10–340 K are reported.

2. Experimental procedure

2.1. Irradiation procedure

Commercial grade PP (Polypenco Ltd, UK) was used in the present investigation. Samples of approximately 0.01 m long and 0.01 m diameter cut from a PP rod were irradiated in air at room temperature with γ radiation from a ^{60}Co source at a dose rate of 0.26 Mrad h^{-1} (1rad = 10^{-2} gray) at the Cotton Textile Research Laboratory (CTRL) Bombay, India. The samples were irradiated to various doses, such as 25, 50, 100, 250, and 500 Mrad. After irradiation samples were kept in a box which was constantly exposed to air.

2.2. Infrared spectra

The infrared (IR) spectra of powdered samples mixed with nujol were recorded by Schimatzu IR spectrophotometer. The IR spectra of an unirradiated sample and for the sample irradiated to 500 Mrad are shown in Fig. 1 from which it can be seen that the degradation also takes place during irradiation in the presence of air. In the IR spectrum of PP which was irradiated to 500 Mrad, the extra bands are observed at about 3400 cm^{-1} (–OH group) and at about 1720 cm^{-1} (carbonyl group) were due to oxidative degradation of the sample [14, 15].

2.3. Crystallinity measurements

Crystallinity changes induced by irradiation were found by X-ray diffraction using a Philips model PW-1050/70 diffractometer with nickel-filtered CuK_α radiation. The X-ray diffraction patterns taken for the powdered samples irradiated to various dosages are shown in Fig. 2. The ratio of the area of the crystalline scattering peak to the total scattering area is taken as the crystallinity index. The variation of the crystallinity index as a function of radiation dose is shown, in

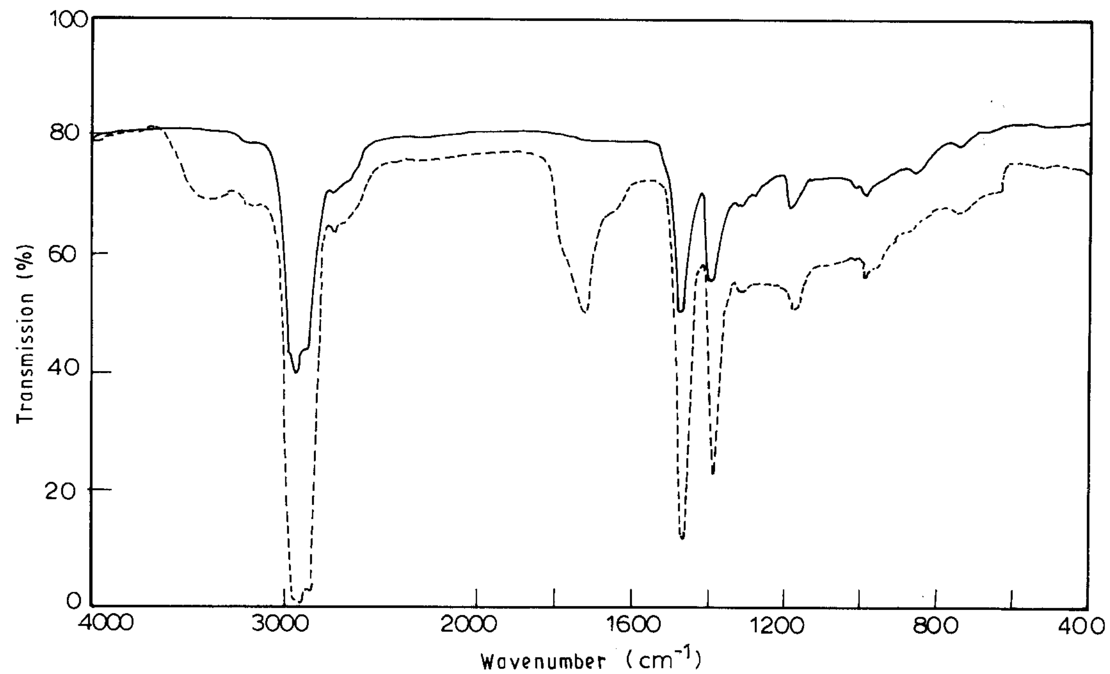

Figure 1 IR spectra of polypropylene samples subjected to (———) 0 and (– – –) 500 Mrad γ radiation.

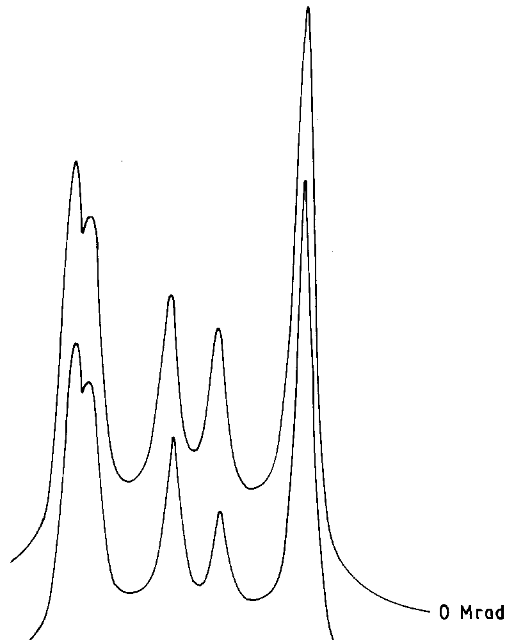

Figure 2 X-ray diffraction pattern of samples of polypropylene subjected to irradiation of 0 and 500 Mrad.

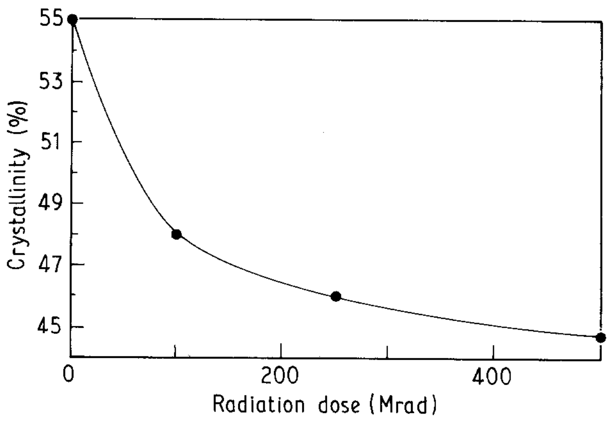

Figure 3 Variation of crystallinity of polypropylene with radiation dose.

Fig. 3, to decrease from 0.55 at 0 Mrad to 0.447 at 500 Mrad. The decrease in crystallinity is a result of cross-linking in the amorphous region as well as on the crystalloid surfaces. The size of the crystallites decreases as the cross-linking takes place, from the surface to the interior part of the crystallite and hence the crystallinity decreases with dose. The decrease in crystallinity is confirmed by the shift of the melting peaks for irradiated PP and by density measurements [6, 16].

2.4. Thermal expansion apparatus

The coefficient of thermal expansion of samples of PP was measured by the three-terminal capacitance technique, described in detail elsewhere [17]. In this technique the changes in length of the sample are converted into changes in electrical capacitance, which is measured, using a six decade ratio transformer bridge, to a resolution of 1 p.p.m. [18]. The capacitance cell is shown in Fig. 4. The capacitance plate, C2, is surrounded by a guard ring, G, which is earthed. The capacitor plate, C1, is connected to the high potential side and C2 to the low potential side of the ratio transformer. Plate C1 rests on Sample S, and C1 is fixed by three symmetrically fixed springs to the base plate, BS. By raising or lowering sample platform, SP, the capacitance gap can be varied. By adjusting the nuts, N, the parallelism of the capacitor gap can be adjusted. Mica sheets of thickness 3×10^{-6} m, are used to insulate Plate C2 from the guard ring, G, and C1 from the body of the cell. The cell is suspended by using nylon thread inside the copper chamber, 4, which is filled with helium exchange gas. The copper chamber, 4, is mounted inside another metal chamber which is immersed in a liquid helium

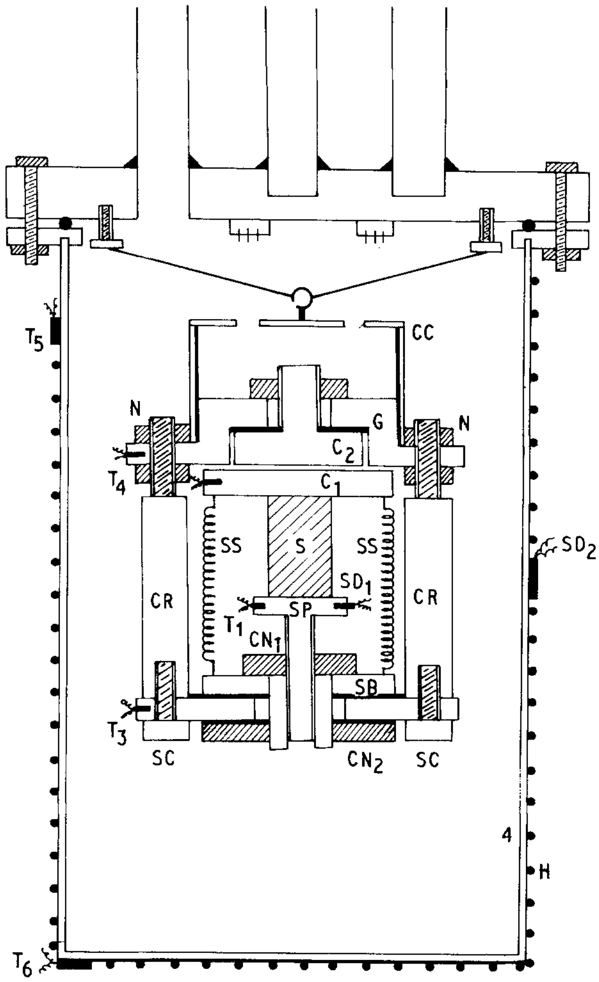

Figure 4 Schematic diagram of a capacitance cell. C1,C2, capacitor plates; SD1, SD2, silicon diodes; SS, stainless steel springs; SP, sample platform; G, guard ring; N, nuts; T1–T6, copper–constantan thermocouples.

bath. The capacitance is measured by using a six-decade ratio transformer bridge developed in our laboratory [19]. The EG & G PARC lock in amplifier model 124A is used as a null detector of the bridge. It has a sensitivity of 100 nV and a built-in oscillator which provides a sinusoidal signal of 10 V r.m.s. and 5 kHz to excite the bridge. The temperature of the sample was measured and controlled to a resolution of 0.05 K by a Lakeshore Cryotronics digital thermometer/controller model DRC-82C, using silicon diode SD1 mounted just below the sample and silicon diode SD2, on the copper chamber, which served as a controller. The 25 Ω heater element was wound around the copper chamber. The thermal gradients across the cell and the sample were measured by the copper–constantan thermo couples, T1, T2, T3, and T4.

2.5. Measuring procedure

The samples were cut into the required size and shape and the two surfaces were made flat and parallel. They were then mounted in the capacitance cell and cooled to liquid helium temperature over a period of 15 h. The samples were heated in steps of 5 K by using the temperature controller. For every stabilized temperature, measurements were taken only when the gradients in the temperature across the sample and any two sections of the cell were less than 0.25 K. The ratio transformer bridge was balanced and the readings giving $1/C$ directly were taken. Thus a set of values of T and $1/C$ were recorded in the temperature range 10–340 K for PP samples irradiated to 0, 200, and 500 Mrad. The thermal expansion coefficient was then calculated by using the relation

$$\alpha_s = \frac{L_c}{L_s}\alpha_c - \frac{0.156\,25}{L_s}\frac{d}{dT}\left(\frac{1}{C}\right) \qquad (1)$$

where L_s is the length of the sample and L_c is the corresponding length of the cell, α_c is the expansivity of the cell which is determined by calibration of the capacitance cell using two NBS standard reference materials, aluminium and germanium. We fitted the α_c values to a polynomial. The coefficients of the polynomial for α_c are given below

$$\begin{aligned}\alpha_c &= 0.805\,3076\times10^{-6} + (-0.181\,7793\times10^{-6})T\\ &+ (0.143\,3447\times10^{-7})T^2 + (-0.496\,6031\times10^{-9})T^3\\ &+ (0.117\,2052\times10^{-10})T^4 + (-0.163\,0323\times10^{-12})T^5\\ &+ (0.126\,3955\times10^{-14})T^6 + (-0.505\,927\times10^{-17})T^7\\ &+ (0.813\,7207\times10^{-20})T^8 \qquad 10\text{ K} \leqslant T \leqslant 120\text{ K} \qquad (2)\end{aligned}$$

$$\begin{aligned}\alpha_c &= (-0.674\,852\times10^{-5}) + (0.143\,7273\times10^{-6})T\\ &+ (0.195\,7517\times10^{-8})T^2 + (-0.288\,9599\times10^{-10})T^3\\ &+ (0.157\,4044\times10^{-12})T^4 + (-0.448\,5718\times10^{-15})T^5\\ &+ (0.674\,5635\times10^{-18})T^6 + (-0.425\,0168\times10^{-21})T^7\\ &77\text{ K} \leqslant T \leqslant 350\text{ K} \qquad (3)\end{aligned}$$

Numerical differentiation and graphical methods of finding $(d/dT)(1/C)$ generates much scatter. An accurate method is to fit the data into a suitable polynomial and differentiate it to obtain the derivative. We have used the spline approximation because of its distinct advantages [20]. By using NAGLIB subroutines E02BAF, E02BBF, E02BCF, the data of $1/C$ versus T were fitted into least square cubic splines and the derivative $(d/dT)(1/C)$ was determined at the experimental temperatures.

3. Results and discussion

The thermal expansion coefficient (α), for the samples irradiated to 0, 250 and 500 Mrad were measured as a function of temperature and the results are shown in Fig. 5. The variation of relative length ($\Delta l/l$) for samples irradiated to 0 and 500 Mrad as a function of temperature is shown in Fig. 6, while the variation of α as a function of dose at different temperatures is shown in Fig. 7.

From Fig. 5 we observe that α is almost constant with radiation dose from 10–125 K. From 125–340 K, however, α decreases with dose, but there is no appreciable change in α for the 0 and 250 Mrad samples with respect to temperature.

The constancy of α of PP samples with radiation dose from 10–125 K is due to the freezing of the

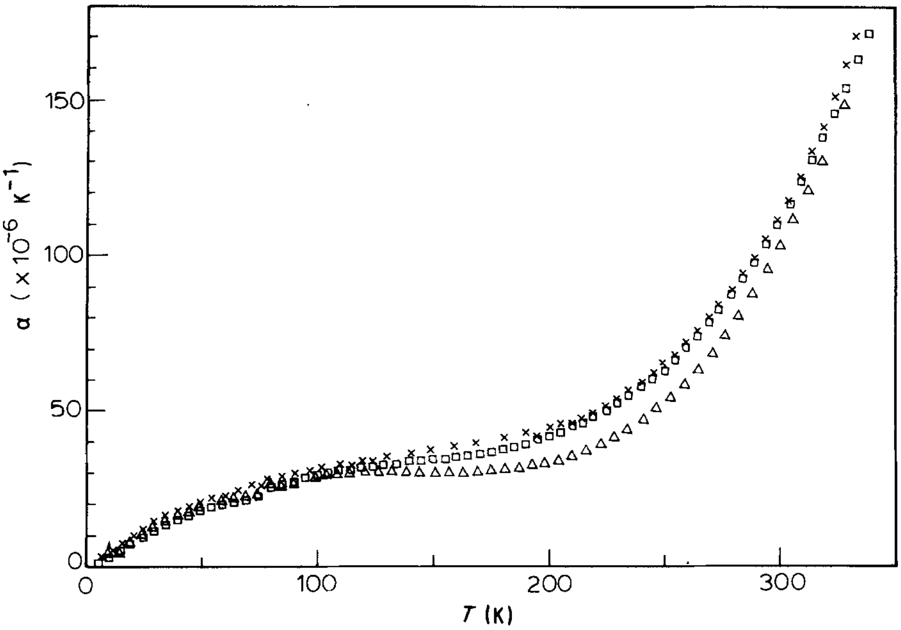

Figure 5 Variation of α of polypropylene with temperature. (×) 0 Mrad, (□) 250 Mrad, (△) 500 Mrad.

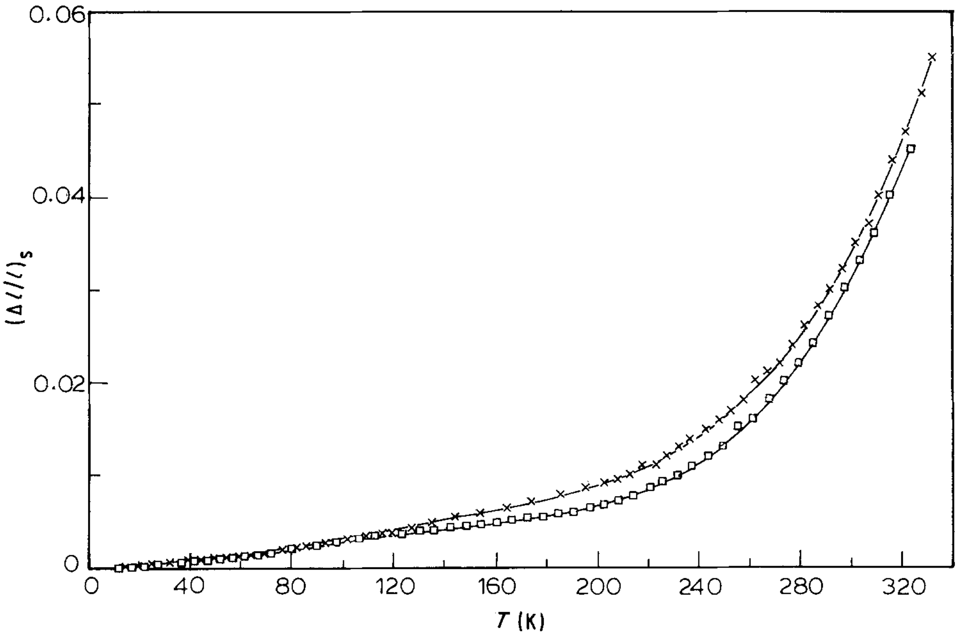

Figure 6 Variation of $\Delta l/l$ of polypropylene with temperature. (×) 0 Mrad, (□) 500 Mrad.

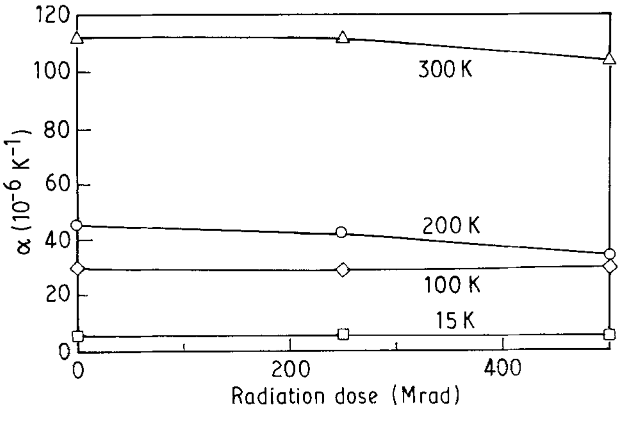

Figure 7 Variation of α of polypropylene with radiation dose.

macromolecules at low temperatures. The radiation cross-linking of the polymer has no influence on its thermal expansion because it is frozen [21]. From 125–340 K, α decreases for the sample irradiated to 500 Mrad, due to cross-linking between linear macromolecules, forming covalent bonds. The number of covalent bonds increases with radiation dose, due to cross-linking. α depends upon the type of bonding between the constituent molecules/atoms, and is larger for van der Waals-type than for covalent-type bonded solids. Hence, α decreases with radiation dose. This conclusion is supported by the work of Wang *et al.* [22]. As the draw ratio increased, the expansivity in the draw direction, $\alpha_{\|}$, decreases, while the expansivity in the perpendicular direction, $\alpha_{\perp}$, increases. With an increase in the draw ratio, the polymer chains become aligned along the draw direction so that the relative increase in inter-chain covalent bonds causes a decrease in $\alpha_{||}$. Radiation-induced cross-linking plays a similar role in the decrease in expansivity. However, the expansivity is nearly the same for samples of PP irradiated to 0 and 250 Mrad, and this is not fully understood.

Acknowledgements

The authors thank CTRL Bombay for providing the radiation facility, and ISRO-IISc Space Technology Cell for financial assistance.

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Received 6 January
and accepted 8 October 1992