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Thermal expansion of irradiated nylon-6 from 10 K to 340 K

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Abstract. Thermal expansion of irradiated nylon-6 has been studied in the temperature range 10 to 340 K using a three-terminal capacitance bridge technique. Irradiation is carried out using cobalt-60 γ-rays up to 500 Mrad dosage. Radiation enhances chain scission over crosslinking. α increases from 0 to 250 Mrad between 10 to 340 K and not much variation is observed between 250 to 500 Mrad for samples from 10 to 250 K.

Keywords. Thermal expansion; low temperature; γ-irradiation; nylon-6; polymer.

1. Introduction

Study of the thermal properties of irradiated polymers is very important from both scientific and technological points of view. Very little information is available on thermal properties like thermal conductivity, specific heat and thermal expansion of irradiated polymers. Thermal expansion of some of the technologically important polymers were studied after exposing the samples to high energy radiation (Subrahmanyam and Subramanyam 1987; Jayanna and Subramanyam 1992, 1993). No thermal properties are studied for irradiated nylon-6. We have made an attempt to measure thermal expansion of irradiated nylon-6 from 10 K to 340 K.

Polyamides have been exposed to a variety of high energy radiations and various physical and chemical changes have been studied by researchers and these are summarized by Zimmerman (1972). It has been observed that on irradiation crosslinking and chain scission occur simultaneously in nylon-6 and its co-polymer. These effects are due to the formation of free radicals, which are on the alpha carbon atom. Also due to the amide nitrogen and steric reasons, chain scission predominates over cross linking. Mechanical properties of nylon-6 fibres irradiated by cobalt 60 γ-ray source to the 10 Mrad level were studied by Ellison *et al* (1984). They found that the tensile strength and elongation at break of the fibre decreases with radiation dose. These effects are due to main chain scission.

Intrinsic viscosity of nylon-6 was measured by Gupta *et al* (1988) and they observed that the intrinsic viscosity [η] first decreases and then increases for the sample irradiated in inert atmosphere. However, irradiation in air decreases the viscosity rapidly. This suggested that main chain scission occurs predominantly upon irradiation in air and chain scission and crosslinking takes place simultaneously on irradiation in inert atmosphere.

2. Experimental procedure

2.1 *Material*

The samples are in the form of rods as received from Polypenco (UK). The samples

are cut into required length of about 1 cm and about 1 cm diameter. The samples were irradiated with cobalt-60 γ-ray source in air at room temperature at a dose rate of 0·25 Mrad/h at the Cotton Textile Research Laboratory (CTRL), Bombay. The samples were irradiated up to 500 Mrad dosage. After irradiation the samples were continuously exposed to air.

2.2 *Measurements*

The melting temperatures of the unirradiated and irradiated samples were measured using Perkin Elmer DSC-2 model. Runs were conducted on samples of about 10 mg at a heating rate of 10°C/min. The melting point of nylon-6 samples with radiation dose is given in table 1.

The X-ray diffraction pattern of the irradiated samples was measured by using Philips model PW–1050/70 diffractometer with nickel filtered CuK_α radiation. The X-ray diffraction pattern was taken for the powdered sample. The diffraction pattern shows the amorphous nature of the sample. The X-ray diffraction pattern for unirradiated sample is shown in figure 1.

Thermal expansion of samples was measured by using three-terminal capacitance technique which is explained in detail elsewhere (Subrahmanyam and Subramanyam

Table 1. Melting point of nylon-6 samples irradiated to different radiation doses.

Radiation dose (Mrad)	Melting point (°C)
0	262·8
100	214·5
200	208·7
500	195·7

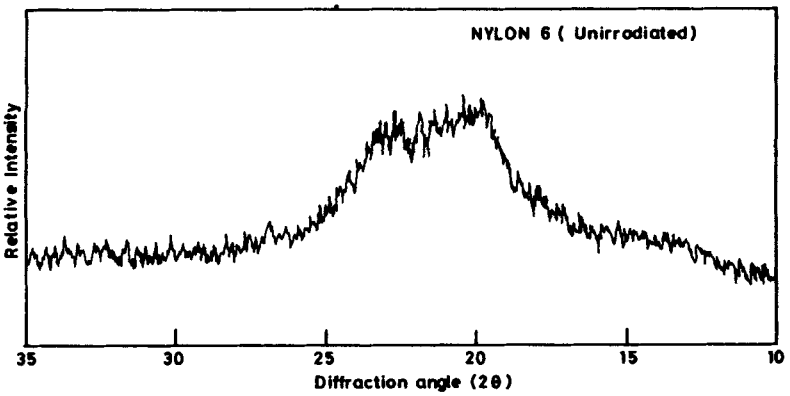

Figure 1. X-ray diffraction pattern of unirradiated nylon-6.

1986). Thermal expansion coefficient (α) has been measured for nylon-6 samples irradiated to 0, 250 and 500 Mrad in the temperature range 10 K to 340 K. The variation of α with temperature is shown in figure 2. The variation of α with dose at various temperatures is shown in figure 3.

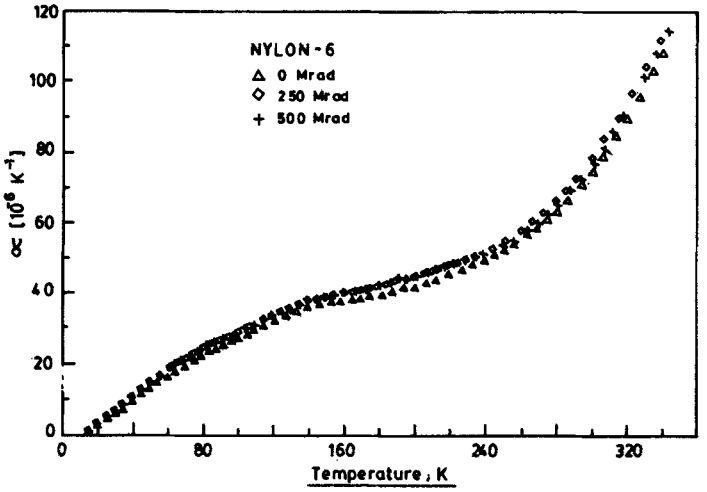

Figure 2. Variation of α of nylon-6 with temperature.

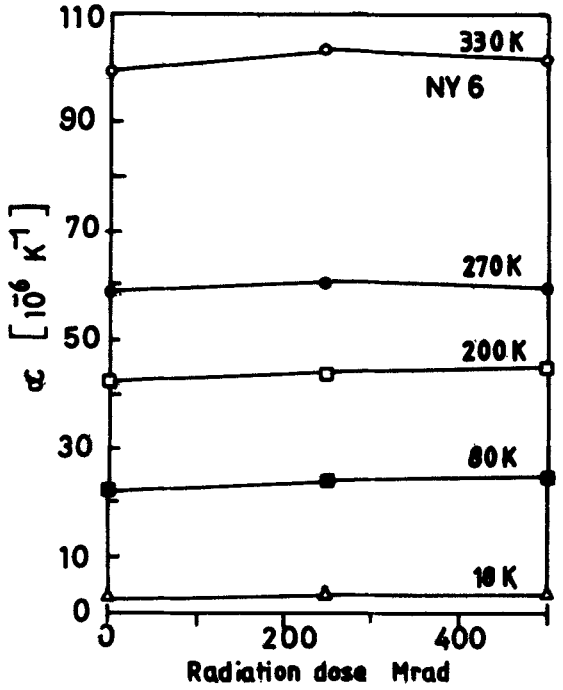

Figure 3. Variation of α of nylon-6 with radiation dose.

3. Results and discussion

From table 1 it is observed that the decrease in melting point of nylon-6 samples with radiation dose is an indication of chain scission predominance over crosslinking.

From figures 2 and 3 it is observed that α increases from 0 to 250 Mrad between 10 K and 340 K, but not much variation is observed between 250 and 500 Mrad samples from 10 K to 250 K. Above 250 K, α values decrease after 250 Mrad. The increase in α is about 3% from 0 Mrad to 250 Mrad samples throughout the temperature range.

As mentioned earlier, chain scission is a predominant process in nylon-6 when it is irradiated in the presence of air. The presence of oxygen in the side group macroradicals may result in decrease in the crosslinking index. The increase in α between 0 and 250 Mrad sample is due to the degradation of nylon-6 during irradiation. For every chain scission, one van der Waal bond will arise. Since the thermal expansion is dependent on the type of interaction between the macromolecules and is large for van der Waal's type bonded solids, α increases with increasing radiation dose. This is also supported by the work of Choy *et al* (1981) and Wang *et al* (1982). The moisture, if present in the sample, is responsible for reduction in interchain interactions (Deopura *et al* 1983) and hence an increase in α.

Invariance of α for 250 and 500 Mrad samples from 10 K to 250 K is due to the competition process between crosslinking and degradation effect on thermal expansion. The decrease in α for samples irradiated to more than 250 Mrad in the temperature range 250 K to 340 K is not understood clearly.

Acknowledgements

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