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Note

THE MELTING BEHAVIOUR OF IRRADIATED POLYMERS

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Differential scanning calorimetry is frequently employed for characterization of minor structural changes in polymers. Recent work to quantify the effects of sterilizing doses of γ radiation on the mechanical properties of medical plastics [1,2], has shown that useful information can be obtained by adopting a double scan procedure separated by a slow cooling or annealing period. High energy radiation affects polymers in a number of ways, particularly through processes of chain scission and cross-linking. As irradiation usually takes place at temperatures at which the material is below T_g or T_m and thus in the solid form, a thermal regime which permits molecular rearrangement can be beneficial in indicating the type of changes which have occurred on irradiation. The information obtained from such procedures, taken in conjunction with mechanical and physical testing results, can be used to predict more precisely the properties of the sterilized component.

EXPERIMENTAL

Samples of Nylon 66 (I.C.I. Maranyl A125) were injection moulded and subjected to radiation doses of 0, 2.5, 5.0, 7.5 and 10.0 Mrad using a cobalt 60 source. The resulting change in average viscosity molecular weight, measured using a single concentration technique [3], is given in Table 1.

The melting behaviour of the material was established using a Du Pont 990 DSC system over the temperature range 20–300 °C, at a heating rate of 10 °C min^{-1}. The tested sample was then allowed to cool back to room temperature in the calorimeter and the experiment repeated. Mouldings were cooled from the melt at a mean rate of greater than 800 °C min^{-1}, whilst recrystallized samples were cooled at a mean rate of 7.5 °C min^{-1}. The crystal content was calculated using a heat of fusion of 197 kJ Kg^{-1} [3]. Tests were carried out under nitrogen and reproducibility of results was confirmed by performing triplicate runs for all materials.

Samples of ultra-high molecular weight polyethylene (UHMWPE, Hoechst Hostalen GUR) used in the manufacture of prostheses, were machined from

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TABLE 1

Effect of irradiation on molecular weight of Nylon 66

Radiation dose (Mrad)	M_v
0	11900
2.5	11600
5.0	14600
7.5	14600
10.0	14700

compression moulded blocks. Moulding conditions resulted in a cooling rate of 1.5 °C min^{-1}. With this material the thermal response between 20 and 200 °C was recorded, again at a heating rate of 10 °C min^{-1}, followed by cooling at a mean rate of 3 °C min^{-1}. The heating programme was then repeated. The degree of crystallinity was calculated from the melting endotherm using a heat of fusion of 291 kJ kg^{-1} [4]. Specimens subject to radiation doses of 0, 2.5, 5.0 and 7.5 Mrad were examined.

RESULTS AND DISCUSSION

With Nylon 66, the irradiation had no effect on total crystal content, confirming results from high dose studies [5,6]. Whilst the recrystallized samples showed similar values to the originals for crystal content, differences were apparent in the form of the melting endotherms. Figure 1 illustrates this for an unirradiated sample. With the injection moulded specimen the small exotherm evident before melting is assumed to be associated with a recrystallization process [7] which is rapidly interrupted by the main melting event. In contrast the recrystallized material does not show the initial exotherm but exhibits two distinct endothermic events. These can be ascribed to the melting of the α_1 and α_2 crystal phases, respectively [8]. Figure 2 shows the effect of increasing radiation dose on the α_1 peak. It is apparent that the definition and size of the peak decreases with increasing dosage. No changes were noted in the form of the α_2 peak, though a slight reduction in the maximum endotherm temperature was observed with increasing dose.

Changes in mechanical behaviour on irradiation have been explained [1] in terms of chain scission and cross-linking. It is suggested that the disorder introduced by these processes hinders the recrystallization of the α_1 phase, limiting both the degree of crystal perfection and the total crystal volume. As the observed changes in molecular weight at low radiation doses are relatively small the results indicate a very high sensitivity of the more closely packed α_1 phase to the small amounts of chain disorder introduced.

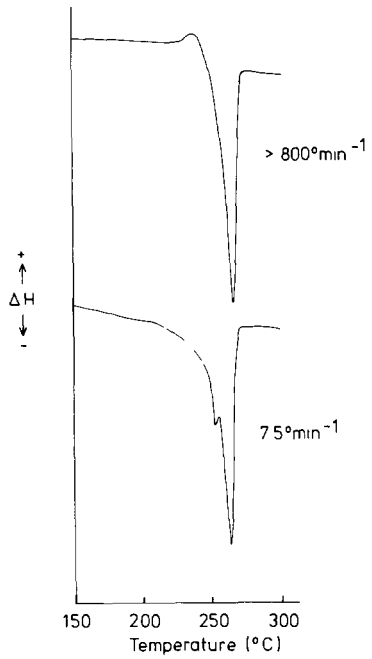

Fig. 1. Effect of cooling rate on subsequent melting endotherm.

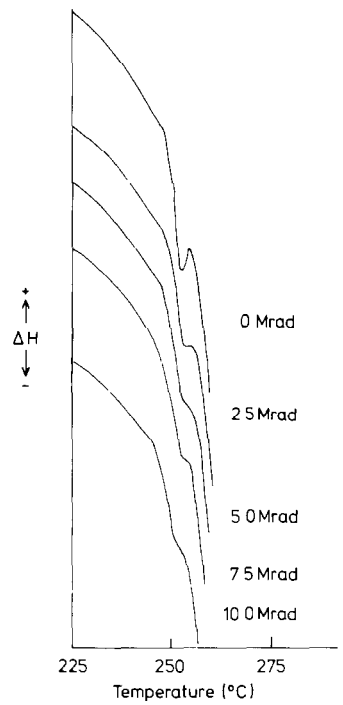

Fig. 2. Effect of irradiation on α_1 peak.

TABLE 2

Melting characteristics of UHMWPE

Radiation dose (Mrad)	Crystallinity (%)	Melting temp. (°C)	Secondary transition (°C)
0	38.5	135	–
0 recrystallized	42.2	134	–
2.5	39.6	134	87
2.5 recrystallized	39.5	130	–
5.0	47.0	136	94
5.0 recrystallized	42.5	129	–
7.5	44.6	137	76
7.5 recrystallized	40.0	130	–

Unlike the Nylon 66, UHMWPE shows no significant change in the shape of the main melting endotherm either with radiation, or on recrystallization, and the results are therefore summarized in Table 2.

The very high molecular weight of this polymer results in extensive chain entanglement, which limits chain mobility, and thus results in relatively low degrees of crystallization in moulded samples. The increase in crystallinity with dose is thought to arise from scission of highly strained long tie chain molecules. This removes an inhibition to further lamella growth and the crystal content is increased through crystal perfection. As polyethylene at room temperature is well above its glass transition, chain mobility is adequate for crystal development.

The percentage crystallinity observed in recrystallized irradiated samples is relatively consistent and supports the proposal [9] that no significant cross-linking occurs within the lamella lattice. The secondary melting peak observed has been noted in other studies [10,11] and is believed to represent a crystal transition from orthorhombic to hexagonal. The decrease in lattice perfection following irradiation reduces the enthalpy of the orthorhombic phase and the transition occurs at temperatures below the melting point. On re-melting the secondary peak disappears as the recrystallized material assumes the more stable orthorhombic form.

Nylon 66 and UHMWPE are two dissimilar semi-crystalline polymers exhibiting different reactions to high energy radiation. With nylon, scission and cross-linking processes compete, whilst in polyethylene cross-linking clearly predominates. In both cases useful information was obtained from the recrystallization technique described.

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