Changes in the crystalline content of irradiated linear polyethylenes upon ageing

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A previous paper[1] reported an unusual 'crystallinity effect' in linear polyethylenes. It was found that ultra high molecular weight polyethylene (UHMW PE) undergoes a significant increase in the degree of crystallinity upon exposure to high energy radiation. The present communication presents some preliminary data on another surprising effect, namely the 'ageing effect', in irradiated linear polyethylenes. The degree of crystallinity in irradiated UHMW PE and irradiated high density polyethylene (HDPE) both was found to rise further upon ageing at ambient conditions.

Keywords Polyethylenes; radiation; ageing; crystallinity; melting

Introduction

A previous paper[1] described an unusual 'crystallinity effect' ovserved in linear polyethylenes. It was found that ultra high molecular weight linear polyethylene (UHMW PE) experiences a significant increase in the degree of crystallinity upon exposure to β-radiation; the corresponding increase in conventional high density polyethylene (HDPE) was much smaller. This crystallinity effect was quite unexpected and surprising, especially in view of the existing literature on the irradiation of polyethylene[2-9]. None of these references mentions anything about the crystallinity effect in polyethylene. In fact, all the references primarily discuss either crosslinking[2-15] or a decrease in crystallinity[16-20] of polyethylene upon irradiation.

The present communication presents some preliminary data on another unexpected and surprising effect in irradiated polyethylenes that recently came to light. It was accidentally discovered that irradiated polyethylenes exhibit an 'ageing effect' whereby their heat of fusion, and hence their degree of crystallinity[21,22], increases monotonically with ageing time at ambient conditions ($\sim$23°C air).

Experimental

Materials. The materials examined in the present communication together with some of their physical and thermal characteristics are listed in *Table 1*.

Sample preparation. The as-received polymer powders were conventionally compression moulded into approximately 3.2 mm thick sheets according to the procedure described elsewhere[1]. Irradiation was carried out in a van de Graaff accelerator at ambient conditions with 2 meV electrons and a beam current of 250 μamp. Radiation doses up to 128 Mrad were used. The irradiated sheet samples were then aged at ambient conditions for varying lengths of time up to 31 months.

Sample evaluation. All samples were evaluated in a Perkin-Elmer differential scanning calorimeter (d.s.c.-2). All specimens, approximately 3 mg in size, were scanned at the rate of 10°C min^{-1}. The heat of fusion, h_f, was derived directly from the d.s.c. scans. The maximum specimen-to-specimen variation in h_f was ± 5 J/g, although generally the scatter was much less. The degree of crystallinity, C, was calculated by assuming the heat of fusion of perfectly crystalline polyethylene to be $\sim$291 J/g. The results are presented in the form of heat of fusion, h_f, as well as per cent crystallinity ($C \times 100$).

Results and Discussion

For both materials, the effect of radiation dose on the heat of fusion and per cent crystallinity is shown in *Figure 1* for three different ageing times. Several interesting features need to be pointed out from these data. Firstly, both materials experience, upon irradiation, an increase in the heat of fusion and per cent crystallinity, the increase being a function of the irradiation dose. In fact, at any given ageing time, h_f and C both increase monotonically up to a certain dose ($\sim$16 Mrad) and then level off or decrease with further increase in dose. Secondly, both materials show a definite 'ageing effect' in that, at any given radiation dose, h_f and C increase monotonically with increasing ageing time (except for HDPE at high radiation doses which probably is a manifestation of

Table 1 Materials examined together with some of their physical and thermal characteristics

Material[a]	Reported intrinsic viscosity (dl/g)	Moulded sheet density (g/cm^3)	Crystallinity calculated from Density (%)	Crystallinity calculated from Heat of fusion (%)	Peak melting temperature (°C)
UHMW PE[b]	19.8	0.928	48.6	46.8	134
HDPE	~2.7[c]	0.962	72.9	70.3	136.5

[a] Materials used here are the same as materials A and C of the previous study[1]
[b] Dow experimental resin
[c] Melt index $\approx$0.3; $M_w \sim 207\,000$
[d] The properties reported here are those of a compression – moulding and not the powder

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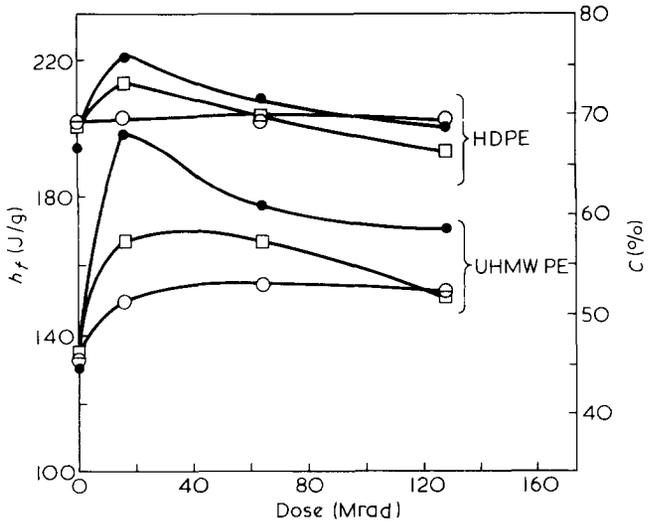

Figure 1 Effect of radiation dose on the heat of fusion of (a) UHMW PE and (b) HDPE for three different ageing times: ⊙, 1 day; ⊡, 9 months; ●, 31 months

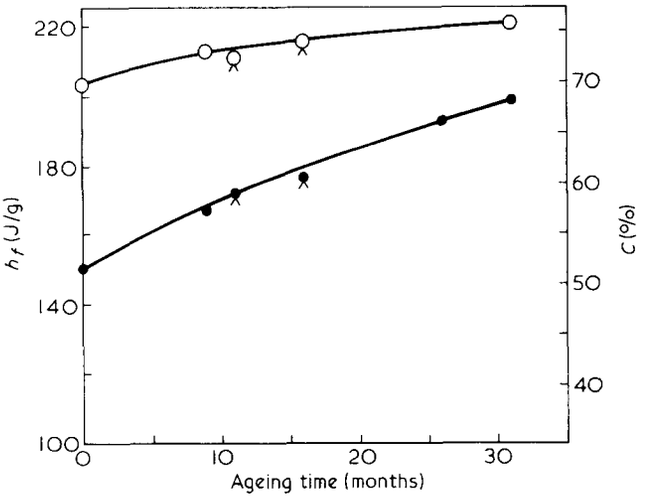

Figure 2 Heat of fusion for both materials (irradiated to 16 Mrad) as a function of ageing time; the data points with a hat are from an independent study[23]: ⊙, HDPE; ●, UHMW PE

extensive degradation). *Figure 2* illustrates the point by showing the variation of h_f and C (at a radiation dose of 16 Mrad) with ageing time. Thirdly, it is interesting to note that the ageing effect continues even after 31 months. And finally, *Figure 1* clearly demonstrates that the magnitude of ageing effect bears a direct relationship to the molecular weight of the virgin, unirradiated samples. For instance, for any given ageing time and radiation dose, the magnitude of increase in h_f or C is much higher in UHMW PE ($M_w > 3 \times 10^6$) than in HDPE ($M_w \sim 2.07 \times 10^5$).

The increase in the degree of crystallinity upon irradiation was explained earlier as resulting from the scission of highly strained molecules (e.g., tie-chain molecules) followed by the subsequent recrystallization of broken chains[1]. It is likely that the ageing effect also involves a similar chain-scission/recrystallization sequence as a function of time. But it is intriguing that the ageing effect persists even after 31 months, especially considering that the crystallization rates in polyethylene at room-temperature are intrinsically very fast. This suggests that the rate-controlling step may be molecular fracture rather than recrystallization. However, it is not clear why molecular fracture should persist after 31 months. Thus, at the present time we do not have a satisfactory explanation for the ageing effect. However, the potential significance of the phenomenon cannot be undermined, especially since the degree of crystallinity governs many of the macroscopic properties of semicrystalline polymers. Additional work is needed to gain a better understanding of the prolonged ageing process. A more complete account of the ageing phenomenon will be published later[23].

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