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Radiation-induced crystallinity changes in polyethylene blends

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It was previously found that upon exposure to high energy radiation, linear polyethylenes experience an increase in the degree of crystallinity [1]. The increase continued monotonically with ageing time [2]. To gain a better understanding of these unexpected results the present paper examines the effects in physical blends of ultra-high molecular weight polyethelyne (UHMW PE) and conventional high density polyethylene (HDPE). No synergistic effects were observed in the blends, but the analysis of the thermal and tensile yield stress data provides some insight into the phenomenon. It provides support for the explanation involving radiation-induced chain-scission followed by recrystallization, and suggests that the chain-scission does not continue with time after initial irradiation.

1. Introduction

Exposure to high energy radiation has been shown to enhance substantially the creep resistance of linear polyethylenes, especially UHMW PE [3]. During the course of that work, two intriguing effects were uncovered, which were termed the "crystallinity effect" [1] and the "ageing effect" [2]. In the first case, UHMW PE and conventional high density polyethylene (HDPE), when exposed in ambient air to high energy radiation, underwent an immediate and significant increase in the degree of crystallinity. In the second case, subsequent ageing of the irradiated materials was observed to cause a further increase in crystallinity.

The magnitudes of these effects were found to be functions of both external and internal variables. For instance, it was found to depend upon the irradiation temperature and dose but not upon the dose rate [4]. Also, the crystallinity rise was shown to increase with increasing molecular weight of the unirradiated materials, being greatest in UHMW PE.

These effects were rather surprising, especially in view of the existing literature on the irradiation of polyethylene [5–10] which discusses primarily two effects: (1) crosslinking and (2) degradation or a reduction in the degree of crystallinity at high radiation doses. To our knowledge, none of the standard references discusses either the crystallinity effect or the ageing effect in polyethylene. This may simply be because these references examined only HDPE materials with *normal* molecular weights; none of them reported on UHMW PE. While linear polyethylenes with normal molecular weights do exhibit the crystallinity and the ageing effects, their magnitudes are small. It is only in UHMW PE that these radiation-induced effects become dramatic. Nusbaum and Rose [11] and Ellis *et al.* [12] in their investigations of radiation-sterilization of UHMW PE did not observe these effects, probably because the radiation doses employed were fairly low (2.5 and 4 Mrad, respectively). Recently, however, Lue *et al.* [13] using higher radiation doses did observe the crystallinity

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TABLE I Materials examined, together with some of their physical, thermal and mechanical properties

Material	Supplier	Reported weight-average molecular weight, M_W	Density of moulded sheets ($g\,cm^{-3}$)	Crystallinity (%) calculated from:		DSC Peak melting temperature (° C)	Tensile modulus ($\times 10^{-2}\,MN\,m^{-2}$)
				Density	Heat of fusion		
UHMW PE	American Hoechst	$> 3.5 \times 10^6$ *	0.934	52.7	50.0	135.8‡	7.6
HDPE	Dow	$\sim 2.07 \times 10^5$†	0.962	72.9	69.8	136.5	11.7

*Measured by light scattering

†Measured by GPC.

‡Properties reported above are those of a moulded sheet rather than the powder itself; the density and peak melting temperature of UHMW PE *powder* are quite high (approximately 0.960 and 141° C, respectively) which is believed to result from the powder being in the extended-chain form.

effect in UHMW PE, as did Roe *et al.* [14], who also observed the ageing effect over a six month period.

The crystallinity effect and the ageing effect are potentially highly significant, especially since the macroscopic properties of semi-crystalline polymers depend critically on the degree of crystallinity. It is, therefore, desirable to understand the nature and origin of these effects. The present paper deals with the irradiation-induced crystallinity and ageing effects in physical blends of UHMW PE and conventional HDPE. Our observations support the concept that irradiation causes scission of strained molecules in the amorphous regions and that chain-scission does not continue with time since irradiation.

2. Materials

The two materials examined in the present work together with some of their physical, thermal and mechanical properties are listed in Table I.

3. Experimental procedures

3.1. Sample moulding

The HDPE and UHMW PE powders in varying proportions were dry blended on a rotating ball mill and the blends compression moulded into 3.2 mm thick sheets according to the following procedure. A weighed quantity of the powder blend was placed within a window mould and subjected to the following moulding sequence:

Moulding temperature; 200° C;

Time at $0.4\,MN\,m^{-2}$ nominal pressure: 5 min;

Time at $6.9\,MN\,m^{-2}$ nominal pressure: 8 min;

Water-cool press platens to 25° C: 4 min;

During cooling, gradually raise pressure to $8.6\,MN\,m^{-2}$ to avoid sink marks.

Release the pressure and recover the moulding.

3.2. Sample irradiation

The sheet samples were exposed at ambient conditions to 2meV electrons in a van de Graaff accelerator. The average beam current used was 250 A and the average dose rate $\sim 0.5\,Mrad\,min^{-1}$. Throughout the present work, only one radiation dose was employed, namely 16 Mrad, the dose at which the magnitude of the crystallinity effect was previously observed to be a maximum [1, 2].

3.3. Sample ageing

The irradiated sheet samples were aged at ambient conditions. Since we were at first unaware of the ageing effect, the 11 and 16 month ageing times used in the present paper were strictly accidental.

3.4. Sample evaluation

All specimens were evaluated in a Perkin-Elmer Differential Scanning Calorimeter, DSC-2. Specimens, approximately 6 mg in size, were heated in the DSC at the rate of $20°\,C\,min^{-1}$ and their heats of fusion, h_f, and peak melting temperature, T_m, were derived. The degree of crystallinity, C, was then calculated as:

$$C = h_f/h_f^0$$

where h_f^0 is the heat of fusion of a perfectly crystalline polyethylene (assumed to be $291\,J\,g^{-1}$ in the present paper). In addition to the thermal response, mechanical behaviour of the blends was also examined. Dumb-bell-shaped specimens were die-cut out of the moulded sheets, preconditioned in the testing environment (23° C and 50% RH) for 48 h and tested in uniaxial tension according to ASTM standard D-638. Nominal tensile yield stress for each sample was then calculated from these data.

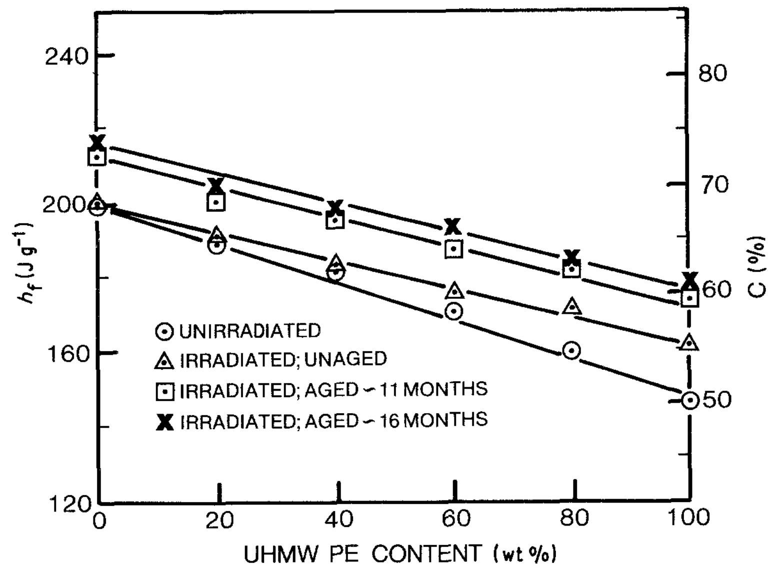

Figure 1 Influence of irradiation and subsequent ageing on the heat of fusion and degree of crystallinity of all the different blends.

An average of three specimens was evaluated at each condition. The *maximum* experimental scatter observed was ± 4 J g^{-1} in h_f, ± 0.8° C in T_m and ± 1.5% in yield stress; generally the scatter observed was at approximately half these values. Thus, the reproducibility in data was surprisingly good, especially considering that the UHMW PE and HDPE powders were simply dry blended and compression moulded, without any extensive mixing in the melt.

4. Results and discussion

It is well-known that linear polyethylene (LPE) crosslinks upon exposure to radiation [5–10]. However, in the present paper we will concern ourselves only with the surprising radiation-induced crystallinity increases for which we will seek satisfactory understanding. Crosslinking and chain-scission have opposing effects on the overall molecular weight of a polymer. The net molecular weight and molecular weight distribution of our irradiated polyethylenes have not been measured. (This is partly due to the difficulties encountered in measuring very high molecular weights associated with UHMW PE [3]; these difficulties are compounded further in irradiated LPE due to crosslinking.) Instead, the data presented below confirm the presence of the crystallinity effect and the ageing effect in many different irradiated polyethylene blends. In addition, the thermal and mechanical data are analysed in terms of a simple model which yields insight into the processes underlying these intriguing phenomena.

4.1. Thermal data: variation of h_f, C and T_m with composition

The variation of heat of fusion, h_f and crystallinity, C with composition for unirradiated, freshly irradiated and aged blends is shown in Fig. 1. The data show cearly the crystallinity effect [11], i.e. an increase in h_f and C immediately after irradiation, the magnitude of the effect being largest for pure UHMW PE and negligibly small for pure HDPE. The data also show the ageing effect [2]. For instance, after 11 months of ageing at ambient conditions, *all* blends including pure HDPE show an additional significant increase in h_f and C. Ageing the blends for an additional 5 months increases h_f and C even further. As an example, the degree of crystallinity of UHMW PE increases from 50% to 55.5% immediately upon irradiation, to 59.4% upon subsequent ageing for 11 months and to 61% upon ageing to 16 months.

Along with the changes in h_f upon irradiation and subsequent ageing, there are concomitant changes in T_m, and these are shown in Fig. 2. For all blends and the two pure polymers, T_m increases significantly immediately after irradiation, but then decreases upon subsequent ageing. Since the average thickness of the crystalline lamellae was found to remain unchanged upon irradiation of UHMW PE and HDPE [1] the initial radiation-induced increase of T_m could not be accounted for by lamellar thickening. Instead, crosslinking in the amorphous regions was invoked as a possible explanation [1, 2]. Whatever is the exact mechanism, its effect is significantly undone upon

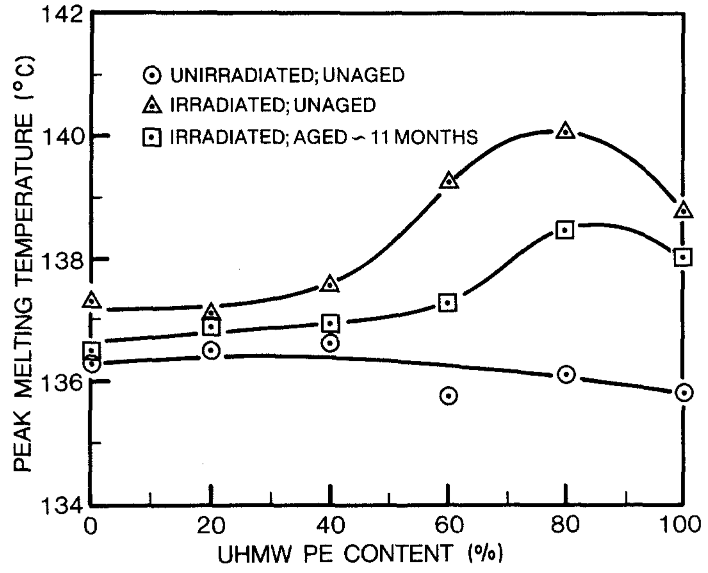

Figure 2 Influence of irradiation and subsequent ageing on the peak melting temperature of all the different blends.

subsequent ageing in that the T_m decreases monotonically with ageing time.

4.2. Analysis of thermal and mechanical data

4.2.1. The model

The thermal data presented above and the yield stress data obtained from uniaxial tensile load–elongation behaviour of the unirradiated, the irradiated and the irradiated and aged samples were analysed in terms of the mechanical model originally employed by Andrews [15] to explain the dependence of yield stress on crystallinity in unirradiated polyethylenes. This model treats polyethylene as a two-phase crystalline/amorphous sandwich structure in which the crystalline lamellae mechanically attached or "welded" at various points, e.g. through very short tie-chain molecules (see Fig. 3). Assuming that the initial yield stress, σ_Y represents the stress required to break down these points of mechanical attachment between the lamellae, the model predicts that

$$\sigma_Y \propto L^2$$

where, $L = C + 0.1$ is defined as the "lamellarity". The factor 0.1 in L accounts for the lamellar fold surfaces, which are amorphous in nature but constitute an integral part of the crystalline lamellae. Indeed a linear relationship between σ_Y and L^2 through the origin was obtained by Andrews for his measurements on unirradiated polyethylenes [15].

4.2.2. Unaged blends

Application of the above model to the analysis of data on the unirradiated and freshly irradiated blends of the present study yields interesting results (see Fig. 4). In both cases, a linear relationship is obtained between σ_Y and L^2. However, the data extrapolate at $L = 0$ to a substantial positive intercept, σ_0^U, for the unirradiated blends and σ_0^I, for the irradiated blends. This is a significant result in that it implies a *finite* yield stress for a completely amorphous polyethylene (i.e. $L = 0$) above its glass-transition temperature. This, of course, cannot be true, but can be explained as as mechanical manifestation of the presence of load-bearing tie-chain molecules outside of the "weld zones" (see Fig. 3). In addition, exposure to 16 Mrad radiation dose is observed to lower

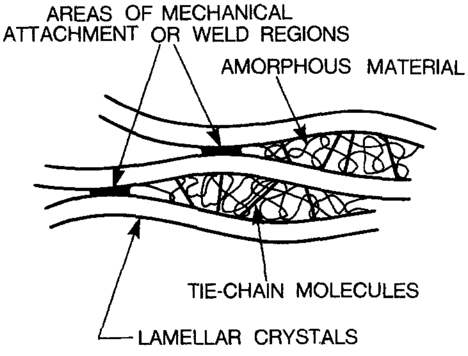

Figure 3 The two-phase crystalline/amorphous sandwich structure modelling polyethylene.

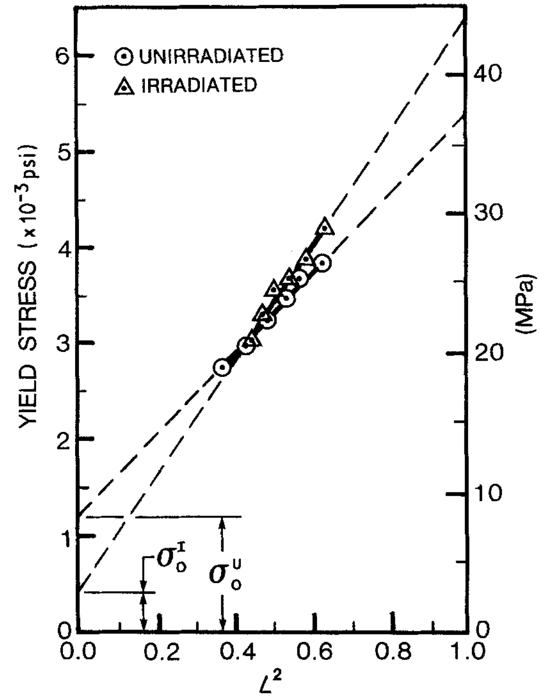

Figure 4 Variation of yield stress with lamellarity^2 for the *unaged* blends: unirradiated; irradiated. (10^3 psi = $6.89 \, \text{N mm}^{-2}$.)

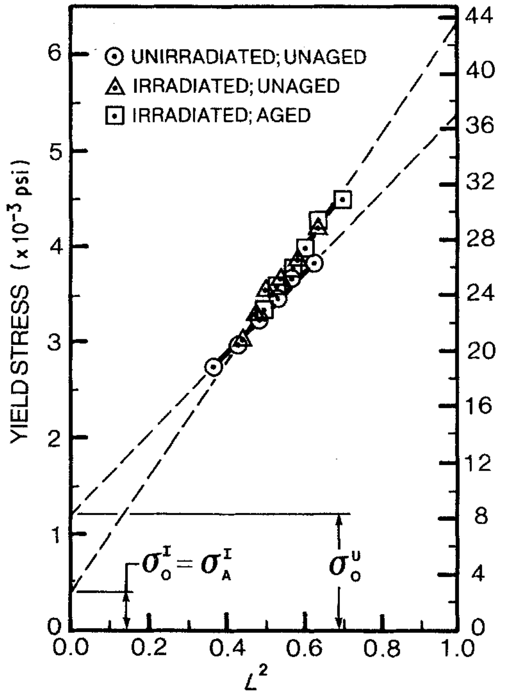

Figure 5 Variation of yield stress with lamellarity^2 for all different blends: unaged, unirradiated; irradiated, unaged; irradiated and aged (16 months).

the intercept on the σ_Y axis, i.e. $\sigma_0^I < \sigma_0^U$. This is quite consistent with the idea that irradiation causes scission of the strained inter-crystalline molecules (e.g. tie-chain molecules). This, in turn, would lower the apparent yield stress at zero crystallinity and thus reduce the intercept.

4.2.3. Aged blends

The effect of ageing the irradiated blends at ambient conditions for 16 months on the plot of σ_Y against L^2 is shown in Fig. 5*, which gives the data for the unirradiated, the irradiated but unaged and the irradiated and aged samples. It should be pointed out that ageing the *unirradiated* blends under identical conditions did not result in any significant change in either h_f or the tensile yield stress.

The interesting feature of Fig. 5 is that the effect of ageing on the plot of σ_Y against L^2 for the irradiated samples is simply to shift all the data points upwards; that is, the plot still remains linear and has the *same slope and intercept* as that for the *unaged* irradiated blend samples. One obvious interpretation of this result is that after the initial scission of strained intercrystalline tie-chain molecules upon irradiation, no additional chain-scission takes place during the ageing process. This result is significant in that it contributes towards our understanding of the ageing process. The data presented thus far clearly support the idea that irradiation causes scission of strained molecules in the amorphous region, allowing further crystallization to occur. However, they do not support the continuation of chain-scission as a function of ageing time.

4.3. Possible explanations for the ageing effect

Physical ageing has been observed in the past in many different polymers, both amorphous [16, 17] as well as crystalline [18–23]. In amorphous polymers, physical ageing is a manifestation of a

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*In an attempt to obtain the tensile yield stress data on the aged, irradiated samples, it was found that the pure HDPE sample and the one with 20% UHMW PE fractured prematurely, before the yield point was reached. Therefore, the σ_Y values for these two samples were obtained by a linear extrapolation of data for the remaining four blends. This is a reasonable extrapolation especially since the data on the other four aged irradiated blends, as well as those for the *unaged* (both unirradiated and irradiated) blends are observed to vary essentially linearly with composition (see Fig. 6).

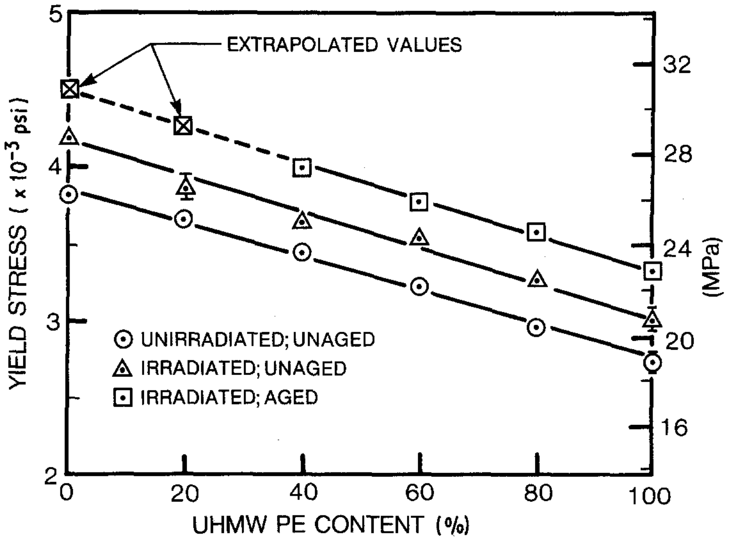

Figure 6 Variation of yield stress with composition for all different blends: unaged, unirradiated; irradiated, unaged, irradiated and aged (16 months).

slow drive towards thermodynamic equilibrium. In crystalline polymers, one of the major factors leading to physical ageing is secondary crystallization. Assuming that the present ageing effect also involves secondary crystallization, we need to examine the exact mechanism causing it. Possible explanations that were advanced earlier [2] are:

1. gradual recrystallization of radiation-scissioned chains over long ageing times;
2. gradual radiation-induced molecular fracture over the long ageing times followed by recrystallization of broken chains;
3. introduction of certain defects (of whatever kind) into the broken chains which, while not preventing further crystallization, hinders and retards it to such an extent that many months are required to complete the process.

The first possibility can be disregarded in view of the intrinsically rapid crystallization rates that are well known to occur in LPE. The second explanation becomes unlikely in view of the data presented above, which suggest that no further chain-scission occurs in irradiated linear polyethylene during the ageing process. Thus, while the exact reasons for this intriguing effect remain unclear, it is possible that irradiation introduces certain defects into the broken chains which can then substantially retard the recrystallization process.

The concept that radiation induces fracture of tie-chain molecules and subsequent recrystallization is extremely interesting since it could provide a simple and convenient tool to study such molecules. By this technique, conceivably one could alter the tie-chain molecular content and hence influence the properties [24]. In addition, it could possibly provide a method of assessing the molecular weight of UHMW PE, which is an extremely difficult task otherwise [25–27].

In conclusion, the data reported in the present paper confirm the presence of the crystallinity effect and the ageing effect in irradiated LPE materials. Analysis of the thermal and mechanical data presented in this paper provides support for chain-scission occurring in LPE immediately after irradiation but not upon subsequent ageing.

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