

Radiation-Induced Crystallinity Changes in Linear Polyethylene: Influence of Aging

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Synopsis

A previous paper described an unusual crystallinity effect observed in ultrahigh molecular weight linear polyethylene (UHMW PE) and conventional high density polyethylene (HDPE). It was discovered that upon exposure to high energy radiation, these polymers experience a significant increase in the degree of crystallinity. The present paper describes another equally unexpected and surprising phenomenon observed in irradiated UHMW PE and HDPE. It was accidentally found that the irradiated polyethylenes exhibit an aging effect; their heat of fusion and hence their degree of crystallinity increases monotonically with the aging time (since initial irradiation) at ambient conditions. Surprisingly, the aging process in irradiated polyethylenes was observed to persist even after 31 months. The magnitude of the aging effect is a strong function of the initial molecular weight of the unirradiated polymers and the irradiation dose. The aging phenomenon could not be accelerated by thermal annealing. The exact mechanisms causing the aging phenomenon remain rather elusive at the present time, but possible reasons are explored.

INTRODUCTION

A previous paper¹ described an unusual "crystallinity effect" observed when ultrahigh molecular weight linear polyethylene (UHMW PE) and conventional high density polyethylene (HDPE) were exposed at ambient conditions to electron beam radiation. For these polymers, the heat of fusion, which is a direct measure of the degree of crystallinity,^{2,3} was found to increase significantly with increasing radiation dose. The increase in the degree of crystallinity upon irradiation, which was confirmed by direct X-ray measurements,¹ will hereafter be referred to as the "crystallinity effect." This effect is interesting, especially since the degree and type of crystallinity govern many of the macroscopic properties of semicrystalline polymers.

The crystallinity effect was quite unexpected and surprising, especially in view of the existing literature. The influence of high energy radiation on the physical, thermal, and mechanical behavior of polymeric materials has been studied extensively during the last few decades and much of this work has been summarized in several different books and review articles.⁴⁻¹⁴ All these references discuss either crosslinking⁴⁻¹⁶ or destruction of crystallinity¹⁷⁻²⁴; none of them mentions anything about the crystallinity effect in polyethylene. (Whether crosslinking occurs in the amorphous or the crystalline regions or both is a controversial issue²⁵⁻³⁰ and will not be discussed here.) Possible reasons for the crystallinity effect were advanced earlier.¹ All the data thus far are consistent with the hy-

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pothesis that irradiation causes scission of tie-chain molecules, which then permits recrystallization of broken chains, resulting in an increase in the degree of crystallinity.

Recently another unexpected aspect of the crystallinity effect came to light.³¹ It was accidentally discovered that the crystallinity effect in linear polyethylenes is time-dependent. In other words, the irradiated polyethylenes were found to exhibit an "aging effect," whereby their degree of crystallinity increased monotonically with aging time at ambient conditions. Surprisingly, the aging effect in irradiated polyethylenes was observed to persist even after ~2.5 years. The nature and origin of the aging effect in linear polyethylenes will form the subject matter of the present paper.

MATERIALS

The materials examined in the present paper are the experimental resins supplied by The Dow Chemical Co. Some of the physical, thermal and mechanical properties of these materials are listed in Table I.

EXPERIMENTAL PROCEDURES

Sample Molding and Irradiation

The polymer powders were compression molded into ~3.2 mm thick sheets according to the procedure described earlier.¹ The sheet samples were exposed to electron beam radiation in a van de Graaff accelerator. Irradiation was carried out at ambient conditions (air, room temperature) using 2 meV electrons and a beam current of ~250 μ amp. Radiation doses D up to 128 Mrad were employed.

Sample Aging

The irradiated sheet samples were accidentally aged at ambient conditions for varying lengths of time, $t \leq 31$ months. Being totally unaware of the presence of the aging effect until relatively recently, all reported values of t are strictly accidental. In fact, measurements at different aging times were not made on

TABLE I
Materials Examined Together with Some of Their Relevant Properties

Material ^a	Designation	Reported Intrinsic Viscosity (dL/g)	Density of molded sheets (g/cm ³)	Peak melting temp (°C)	Crystallinity calculated from:		Young's modulus ($\times 10^{-2}$ MN/m ²)
					Density (%)	Heat of Fusion (%)	
UHMW PE ^b	A	19.8	0.928	134	48.6	46.8	6.9
UHMW PE ^b	B	14.8	0.933	135.5	52.1	47.8	8.3
HDPE ^c	C	2.7	0.958	136.5	72.0	70.3	11.7

^a The materials used in the present study are the same as those in the earlier work.¹

^b Experimental resins.

^c MI ~ 0.3, M_w ~ 207,000.

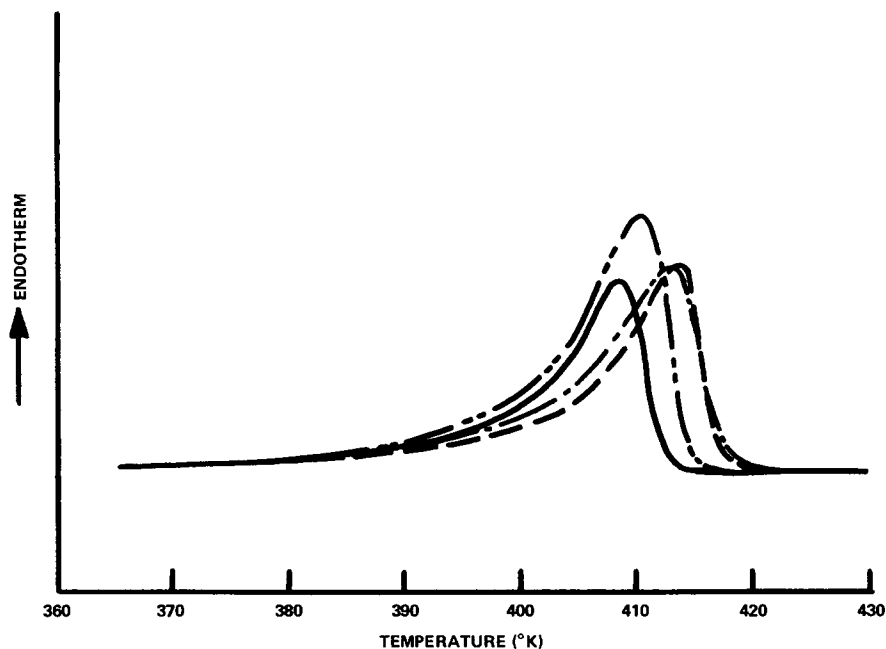


Fig. 1. Effect of irradiation (16 Mrad) and subsequent aging for 1 day (---), 9 months (- · - · -), and 31 months (- - - -) on the DSC thermogram of UHMW PE (A): (—) unirradiated, unaged.

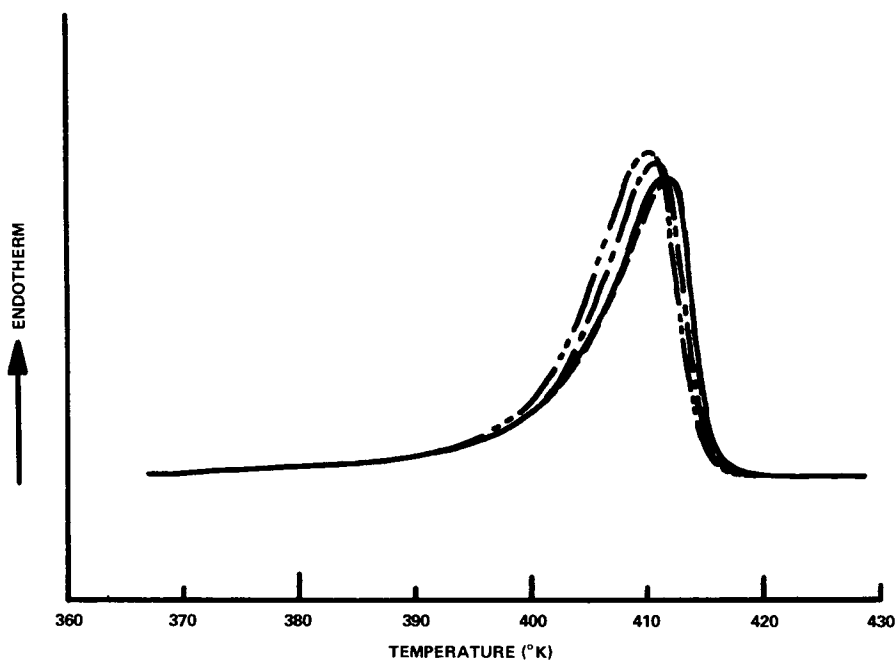


Fig. 2. Effect of irradiation (16 Mrad) and subsequent aging for 1 day (---), 9 months (- · - · -), and 31 months (- - - -) on the DSC thermogram of HDPE: (—) unirradiated, unaged.

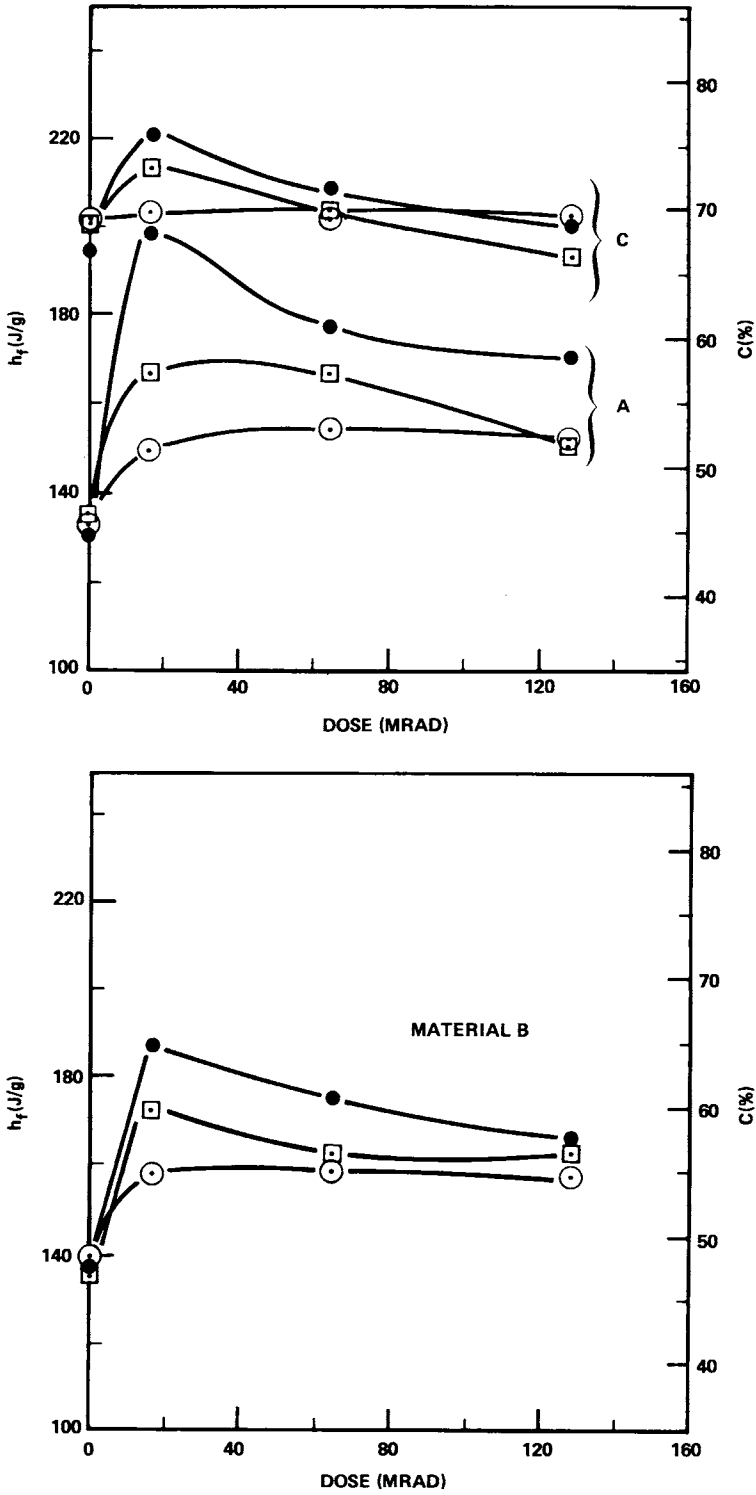


Fig. 3. Effect of radiation dose on the heat of fusion and degree of crystallinity of all three materials at three different aging times: (○) 1 day; (◻) 9 months; (●) 31 months.

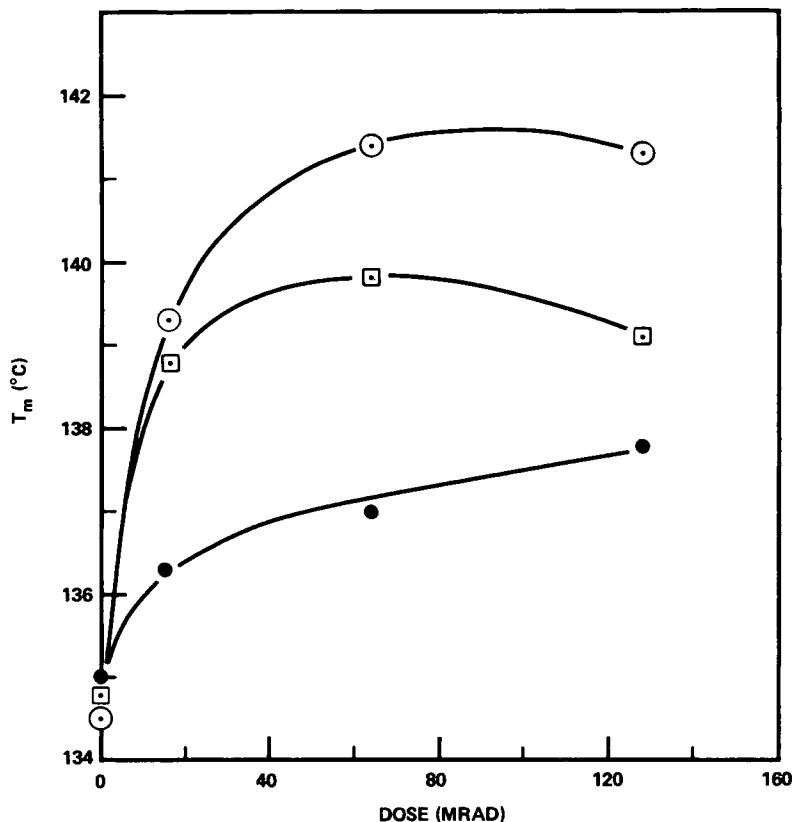


Fig. 4. (a) Effect of radiation dose on the peak melting temperature of UHMW PE (A) at three different aging times: (○) 1 day; (◻) 9 months; (●) 31 months. (b) Effect of radiation dose on the peak melting temperature of HDPE at three different aging times.

specimens from the *same* sheet sample but rather on specimens from different sheet samples which were aged for different lengths of time. However, *all* sheets were molded, irradiated, and aged under identical conditions.

Sample Evaluation

All samples were evaluated in a Perkin-Elmer Differential Scanning Calorimeter (DSC-2). All thermograms were obtained at a scan rate of 10°C/min, using a specimen size of ~3 mg. Since it was shown in the previous paper¹ that the crystallinity effect in polyethylenes is completely lost after first melting, in the present study only the *first* DSC scans were run. From the DSC thermograms, the peak melting temperature T_m and the heat of fusion h_f , were derived. The degree of crystallinity C was calculated as^{32,33}

$$C = h_f/h'_f$$

where h'_f = heat of fusion of a 100% crystalline specimen. For the present work, h'_f was assumed to be ~291 J/g. The data in the present paper are presented in the form of heat of fusion as well as percent crystallinity (= $C \times 100$).

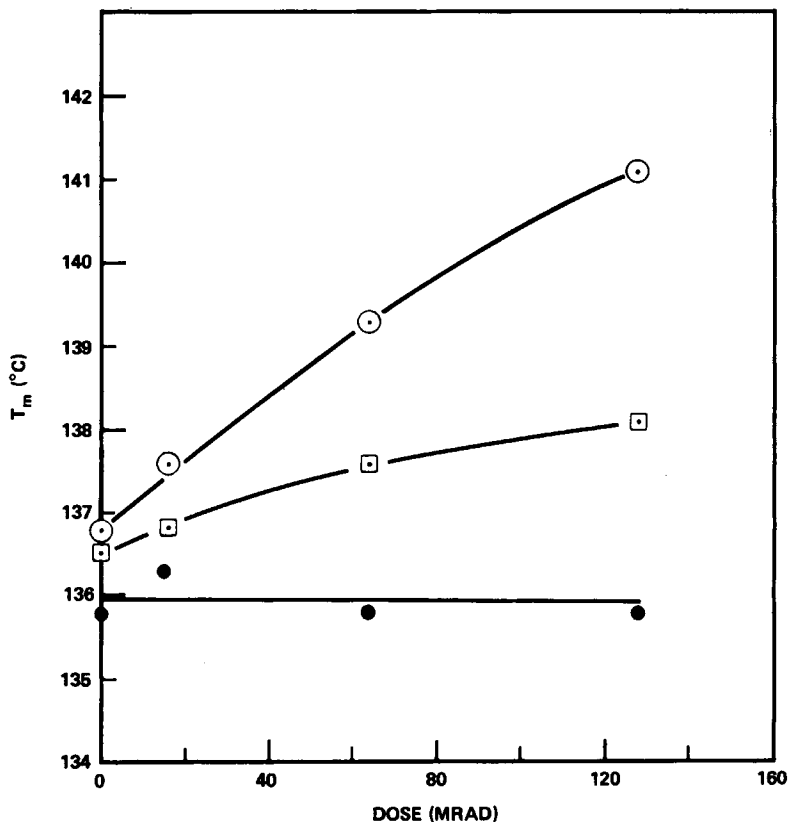


Fig. 4. (Continued from previous page.)

EXPERIMENTAL RESULTS

The effect of irradiation and subsequent aging for $t \leq 31$ months on the DSC thermograms of UHMW PE (material A) and HDPE is shown in Figures 1 and 2, respectively. These data were obtained for a constant radiation dose D of 16 Mrad—the dose at which the crystallinity effect was observed to be a maximum.¹ As can be seen from Figures 1 and 2, irradiation and subsequent aging both significantly influence h_f and T_m in both materials, although the effects are more pronounced in UHMW PE. The variations of h_f and T_m with D and t are presented quantitatively in the next few sections.

Effect of D and t on h_f

For all three materials, the effect of D on h_f (and hence C) for three different aging times is shown in Figure 3. Several interesting features need to be pointed out from these data. First, for all three materials, h_f (and C) are strongly influenced by D . In freshly irradiated materials, h_f and C both rise monotonically with D up to a certain value of D (~ 16 Mrad), and then level off or decrease with further increase in D . Second, all three materials show a definite *aging effect* in that, at any given D , h_f increases significantly with increasing t . Third, it is

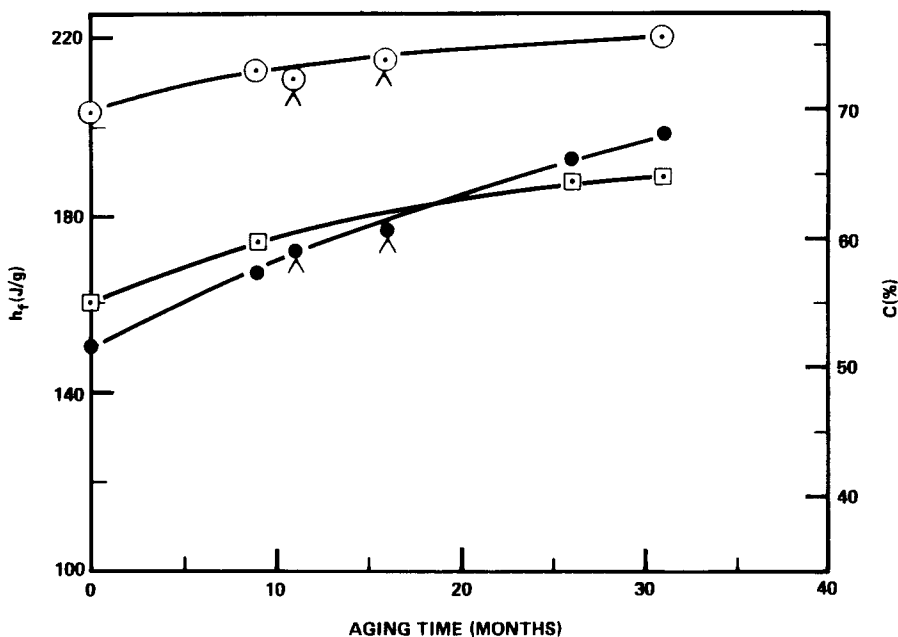


Fig. 5. Effect of aging time on the heat of fusion and degree of crystallinity of all three materials irradiated to 16 Mrad; the data points with a hat are from an independent study on blends³⁴: (○) C; (□) B; (●) A.

interesting to note that h_f continues to rise for $t > 31$ months. It should be noted that the spread in h_f values for the virgin/unirradiated specimens simply represents the inherent scatter in the data.

Effect of D and t on T_m

The variation of T_m with D and t is shown in Figure 4(a) for UHMW PE (A) and Figure 4(b) for HDPE. The results for UHMW PE (B) were similar to those for UHMW PE (A) and hence are not presented here. As can be seen from Figure 4, T_m increases immediately upon irradiation, the magnitude of increase depending upon radiation dose. Since the average lamellar thickness of UHMW PE and HDPE was shown to remain unchanged by irradiation,¹ this increase in T_m cannot be explained by lamellar thickening. It could possibly result from enhanced crystallite perfection caused by irradiation or from crosslinking in the amorphous regions. Whatever the exact reason, this effect is essentially undone upon subsequent aging and T_m decreases monotonically with aging time. This must then, in turn, imply a corresponding decrease in crystallite perfection and that the crosslinks that are formed during irradiation are subsequently oxidizable and labile.

Influence of Initial Molecular Weight on Aging Effect

Figure 3 clearly demonstrates that the magnitudes of the crystallinity effect and the subsequent aging effect are directly related to the initial molecular weight

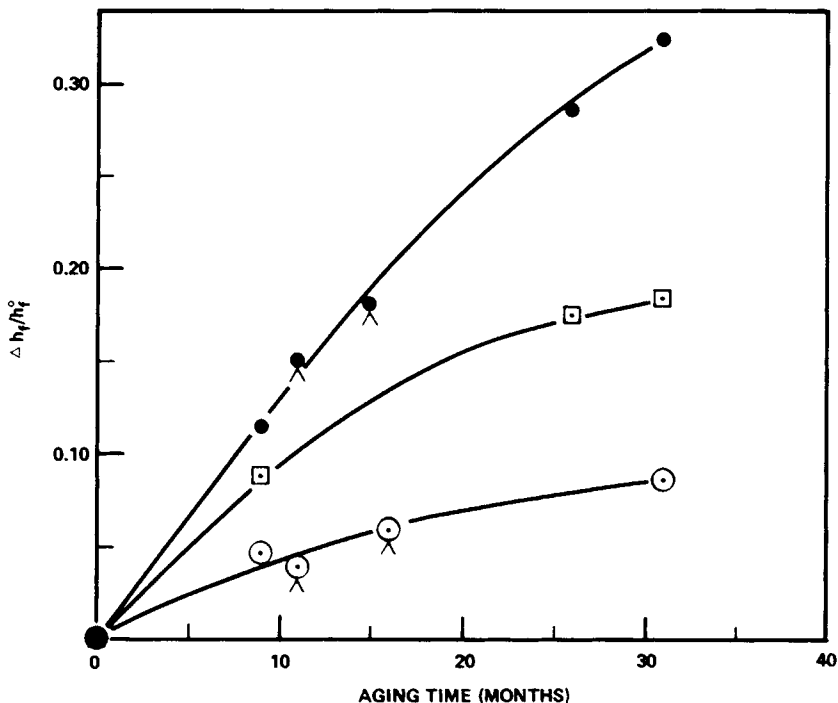


Fig. 6. Effect of aging time on the "normalized" heat of fusion of all three materials irradiated to 16 Mrad; the data points with a hat are from an independent study on blends³⁴: (○) C; (◻) B; (●) A.

of the virgin unirradiated samples. For instance, for any given t , the magnitude of both effects is the largest in UHMW PE material A, which has the highest molecular weight ($M_w > 3 \times 10^6$) and the smallest in HDPE material C, which has the lowest molecular weight ($M_w \sim 0.21 \times 10^6$).

For all three materials, the effect of t on h_f for a given value of D (16 Mrad) is shown in Figure 5. The 11- and 16-month data for UHMW PE material A and HDPE material C from independent experiments on blends³⁴ are also included. As is clear from Figure 5, h_f for all three materials increases monotonically with t . For all three materials, dh_f/dt decreases with increasing t and h_f appears to approach an asymptotic value. That the aging effect bears some sort of a direct relationship with the initial molecular weight can be seen very clearly when the data of Figure 5 are normalized and replotted, and that is done in Figure 6, which plots $\Delta h_f/h_f^0$ vs. t , where $\Delta h_f = h_f - h_f^0$ and h_f^0 = heat of fusion for freshly irradiated, i.e., unaged specimen. Figure 6 shows that the magnitude of the aging effect for all three materials increases monotonically with t and the data tend to approach an asymptotic/equilibrium value at large aging times. This is to be expected since h_f cannot rise indefinitely. Furthermore, the data clearly demonstrate that, for all values of t , the aging effect is a function of the initial molecular weight.

Influence of Thermal Annealing on Aging Effect

In order to examine the possibility of thermally accelerating the aging process, some sheet samples of UHMW PE material A were freshly exposed to a radiation

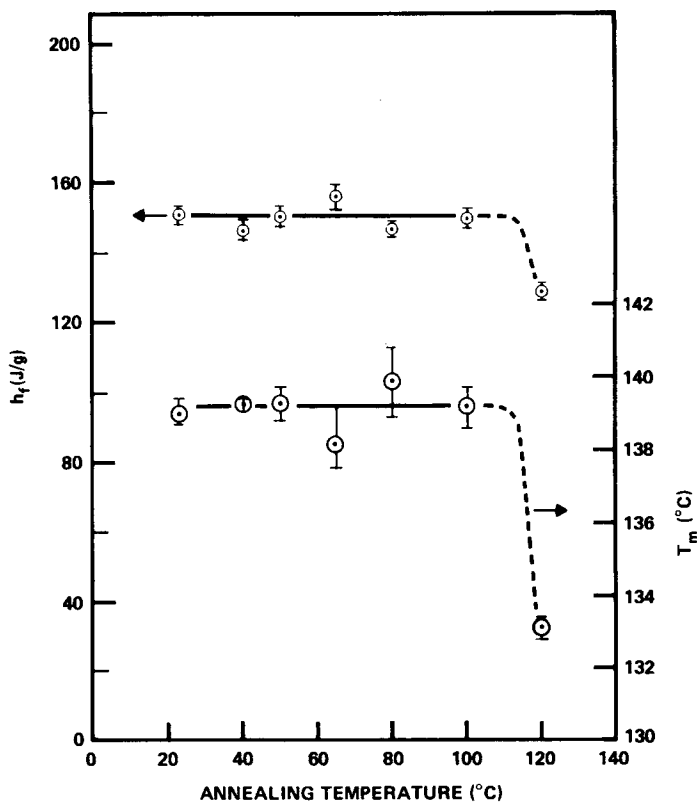


Fig. 7. Effect of annealing temperature on the heat of fusion and peak melting temperature of UHMW PE material A; freshly irradiated specimens (16 Mrad) were annealed at different temperatures for 24 h.

dose of 16 Mrad (the dose at which the crystallinity effect and the aging effect are both a maximum) and immediately annealed at different temperatures in a vacuum oven for ~ 24 h. These samples were then cooled in ambient air and their h_f and T_m were determined. The resulting data are presented in Figure 7 as a function of the annealing temperature. As can be seen from the figure, h_f and T_m both remain relatively unaffected by thermal annealing at temperatures up to 100°C . Annealing at 120°C was found to cause a decrease rather than an increase in h_f and T_m , which is caused by partial melting and subsequent recrystallization. Although it is possible that the samples were not annealed for long enough periods of time (especially since the crystallization kinetics are extremely slow in UHMW PE³⁵⁻³⁸), Figure 7 suggests that the aging process in irradiated UHMW PE cannot be accelerated by thermal annealing at elevated temperatures.

DISCUSSION

The data presented so far clearly demonstrate some intriguing effects that irradiated polyethylenes exhibit: the crystallinity effect, the aging effect, and an increase in T_m upon irradiation followed by a decrease upon subsequent aging. The crystallinity effect can be explained by the two-step process of irradiation causing scission of strained molecules, such as tie-chain molecules, followed by

recrystallization of the broken chains. [At room temperature ($\gg T_g$ of linear polyethylene) sufficient molecular mobility exists for the broken chains to reorganize and recrystallize.] But we are unable to satisfactorily explain the aging effect or the variations in T_m at the present time.

Physical aging has been observed to occur in amorphous polymers over long periods of time.³⁹⁻⁴² Its origin has been explained in terms of the changes in free-volume and segmental mobility caused by relaxation processes, which attempt to establish thermodynamic equilibrium.⁴² Physical aging has also been observed in semicrystalline polymers, where one of the primary factors is the secondary crystallization.⁴³⁻⁵⁰ Assuming that the present aging effect in irradiated polyethylenes involves some kind of secondary crystallization or realignment of chains, several possible mechanisms conjectured are as follows.

The first speculated mechanism, which does not involve chain scission, is based primarily on some kind of annealing process and chain alignment in the amorphous regions. Irradiation introduces crosslinks and microstresses in the amorphous regions. Perhaps the microstresses are relaxed upon subsequent aging through some sort of chain alignment. Crosslinking will decrease the overall chain mobility, which can explain why the alignment/aging process is slow.

In the second possible mechanism (which appears more likely) of chain scission followed by recrystallization, several possibilities can arise. First, the broken chains may recrystallize gradually over long periods of time. However, this is highly unlikely in view of the known intrinsically rapid crystallization rates in linear polyethylenes. This leads to the second possibility that the rate-controlling step may be molecular fracture rather than recrystallization. But it is unlikely that the entrapped free radicals, which lead to molecular fracture, will survive for several years in polyethylene at room temperature. Also, some independent mechanical measurements on irradiated blends of UHMW PE and HDPE suggest that the occurrence of chain scission over long periods of time is unlikely.³⁴ Third, it is possible that certain defects (whatever they might be, including crosslinks) are introduced into the system, which can then significantly hinder the crystallization process and explain, at least qualitatively, the slow aging process.⁵¹ Whatever the exact mechanism involved, additional support for the basic hypothesis (of radiation causing scission of tie-chain molecules followed by recrystallization of dangling chains) comes from the fact that the irradiated polyethylenes have been observed to become increasingly brittle with aging time.

As is obvious from the present discussion, we do not have a satisfactory understanding of the aging effect. Additional work is needed to gain a better appreciation of this unusual effect, before its full potential can be realized. However, the significance of the phenomenon can not be undermined, especially since the degree and type of crystallinity govern many of the macroscopic properties of semicrystalline polymers. If the basic hypothesis is correct, it may provide us a convenient and powerful tool to study and alter the tie-chain molecules. In addition, it may also provide us a simple method for measuring the molecular weight of UHMW PE, which is extremely difficult to measure otherwise.^{52,53}

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