

Electron Beam Irradiation of an Ultrahigh Molecular Weight Polyethylene Resin in Air

W. BRENNER and A. ADLER, *New York University, Department of Chemical Engineering, New York, New York*; H. J. OSWALD and E. A. TURI, *Allied Chemical Corporation, Corporate Chemical Research Laboratory, P. O. Box 309, Morristown, New Jersey 07960*

Synopsis

High molecular weight linear polyethylene has been irradiated in the solid state by high energy electrons. The irradiated samples were characterized by differential scanning calorimetry, solubility properties, and stress-strain measurements. A failure mechanism is proposed for the observed embrittlement of the polymer.

INTRODUCTION

The effect of high-energy ionizing radiation on polyolefins has been the subject of extensive experimental investigations, with particular emphasis on the irradiation response of polyethylenes.¹⁻³ Various reviews of published work, which encompass the exposure of a wide range of both high and low density-type polyethylene to ionizing radiation, emphasize the crosslinking effects of such treatments in terms of resulting polymer characteristics.^{4,5} These polymers have molecular weights in the general range of 20,000-300,000. The irradiation response of the so-called ultrahigh molecular weight polyethylene resins has, however, apparently not been reported on. These polymeric materials are being increasingly utilized for applications where their outstanding resistance of abrasion and wear, impact, chemical attack, and cold flow can be advantageously employed.^{6,7} It is the purpose of this paper to describe and discuss the effects of high-energy electron beam irradiations in air on some pertinent polymer properties of an ultrahigh molecular weight polyethylene resin.

EXPERIMENTAL PROCEDURE

Skived tape (0.008 in. thick) of a commercially available ultrahigh molecular weight polyethylene resin was irradiated in air with high energy electrons from 1.5 meV Dynamitron electron beam accelerator (Radiation Dynamics, Inc., Westbury, N. Y.) This polymer was characterized by a viscosity-average molecular weight of 850,000 g/mole as determined by dilute solution viscosimetry in decalin at 135°C. The molecular weight was estimated from the intrinsic viscosity by the following equation⁸:

$$[\eta] = 6.77 \times 10^{-4}(\bar{M}_v)^{0.67}.$$

The tape samples were subjected to dosages ranging from 5 to 60 Mrads.

The irradiations were conducted by passing polymer tape samples suitably positioned on a conveyor beneath the electron beam. The dosage per pass was 5 Mrads, as determined by cellophane dosimetry. Multiple passes were employed to obtain dosages in excess of 5 Mrads up to 60 Mrads. Approximately 5 min were permitted to elapse between passes in order to minimize heating of the samples due to the applied energy. Selected temperature measurements of the surface of the polyethylene film samples showed that the temperatures during the irradiations did not at any time exceed 40°C.

Tensile properties of the variously irradiated ultrahigh molecular weight polyethylene samples were measured on an Instron testing machine at 23° and 100°C with a 20 in./min head speed. The test specimens were cut from the irradiated tape and tested in accordance with the procedures detailed from long tensile impact (ASTM D1822-61T). The results of these tensile tests are listed in Table I and graphically shown in Figures 1 and 2. Yield stress data are plotted in Figure 3.

The percentage of gel or insolubles was determined in the irradiated samples by dissolving them in a 0.1 wt-% concentration at 170°C in decalin stabilized with 0.1 wt-% phenyl- β -naphthylamine, under the protection of

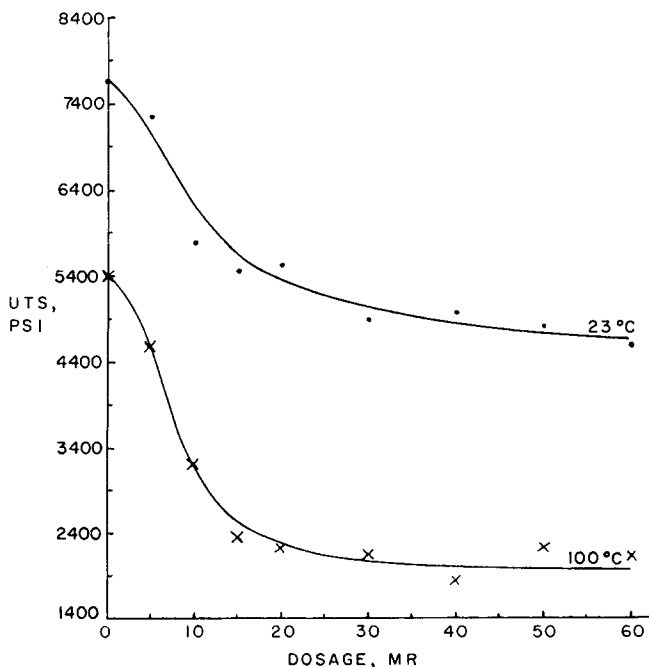


Fig. 1. Ultimate tensile strength vs. irradiation dosage.

TABLE I
Irradiated Polyethylene; Tensile Properties Versus Irradiation Dosage

Tensile properties ^a	Testing temp.	0 (control)	Irradiation dosage, Mrads							
			5	10	15	20	30	40	50	60
UE, %	23°C	1020	1020	720	510	630	320	310	190	150
	100°C	2450	2210	1150	690	590	420	350	210	160
UTS, psi	23°C	7670	7250	5800	5470	5540	4900	4990	4820	4620
	100°C	5420	4590	3210	2370	2210	2140	1850	2230	2130
YS, psi	23°C	3980	3890	3940	3980	3910	4050	4200	4260	4290
	100°C	1350	1560	1540	1630	1720	1680	1720	1960	2040
YE, %	23°C	39.5	39.0	35.2	38.6	40.2	40.3	38.1	39.9	42.3
	100°C	36.1	34.9	36.6	37.7	36.6	35.2	36.7	41.6	43.1
Young modulus, psi	23°C	10200	10900	11300	11200	11100	11700	11300	11800	11400
	100°C	5000	5200	5000	5100	5200	5200	5000	4500	5000

^a Tensile impact, long, 20 in./min head speed; Instron tensile tester.

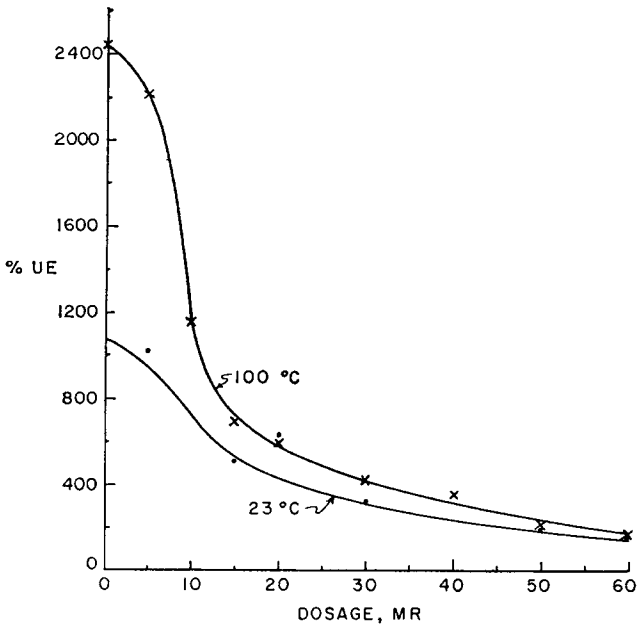


Fig. 2. Ultimate elongation vs. irradiation dosage.

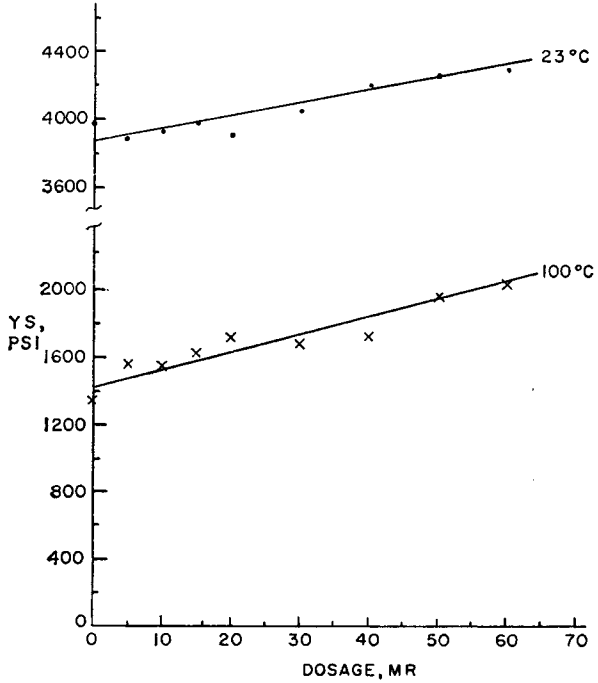


Fig. 3. Yield stress vs irradiation dosage.

a nitrogen atmosphere for 24 hr. The insoluble fraction was removed by filtration, washed repeatedly with acetone, and dried to constant weight at 65°C in vacuo. The soluble fraction was recovered to obtain an internal weight balance. The fraction of insolubles in wt-% is listed in Table II.

The melting and crystallization behavior of the irradiated ultrahigh molecular weight polyethylene samples was studied as a function of absorbed dosage with a Perkin-Elmer differential scanning calorimeter (DSC). The experimental procedure consisted of heating suitable size sample material up to 200°C with a heating rate of 10°C/min, followed by cooling to 35°C at a rate of 5°C/min, and reheating a second time to 200°C, again at a 10°C/min rate. All heating and cooling operations were carried out under a nitrogen atmosphere. The melting points and heats of fusion for the first and also the second heating cycles as well as the temperature of the maximum rate of crystallization, T_c , under cooling conditions as employed, are likewise listed in Table II.

DISCUSSION OF RESULTS

The solid state electron beam irradiation of an ultrahigh molecular weight polyethylene resin in air resulted in a steady deterioration of the mechanical strength properties with increasing dosage, both at ambient and elevated temperatures. Since the same polymer has been exposed to ultraviolet irradiation in an oxidative atmosphere and the resulting degradation of its properties has been studied,⁹ it is tempting to compare the results. Of course, the two conditions of irradiation differ largely and should be kept in mind when the comparison is made. The β -radiation dosages ranged from 5 to 60 Mrads total, or approximately $0.1\text{--}1.2 \times 10^8$ ergs/cm², with the Dynamitron. The incident ultraviolet irradiation was applied at 1.2×10^6 ergs/cm² per sec for the 2800–3200 Å region, using a 450-watt Hanovia high-pressure quartz mercury vapor lamp equipped with a corex filter. The material temperature in the latter case was about 45°C, as compared to below 40°C in the β -irradiation experiments. The total ultraviolet irradiation dosages in the 2800–3200 Å region ranged from 4.3×10^{10} to 6.5×10^{10} ergs/cm² after 100–150 hr of exposure, a factor roughly 100 times higher than in the Dynamitron electron beam experiments.

The high energy electrons will form ozone radiolytically, some of which may react with the sample, although an intensive air circulation was maintained to remove the ozone. It is believed, however, that the ozone reaction was only surface deep as it has been reported that ozone diffusion through polyethylene is extremely slow.¹⁰ The major difference between the two irradiation conditions thus appears to be the energy of incident radiation, the intensity of dose rate, and the duration of the experiment, since both samples have about the same thickness, 10 and 8 mil, respectively. The large difference in solution properties produced by the two modes of irradiation in the same polymer may be traced to the presence or absence of oxygen. During the high-energy electron irradiation the oxygen in the sample

TABLE II
Differential Scanning Calorimetry of Irradiated Polyethylene^a

Irradiation dose, Mrads	Insoluble wt-%	1st Heating cycle ^b		ΔH_f , cal/g	T_c , °C	Cooling cycle ^c		2nd Heating cycle ^b	
		T_m , °C	ΔH_f , cal/g			T_c , °C	$-\Delta H_c$, cal/g	T_m , °C	ΔH_f , cal/g
0		134	37	116		32		132	34
5		134	39	114		29		131	33
10	71.6	135	38	114		26		129	32
15		126 ^d	39	113		26		128	32
20	79.4	127 ^d	38	113		24		128	32
30		125 ^d	39	115 ^d	111	24		126	29
40	83.0	125 ^d	40	115 ^d	111	27		127	30
50		123 ^d	41	113	110 ^d	28		126	30
60	91.4	122 ^d	41	113	108 ^d	26		126	32

^a Perkin-Elmer differential scanning calorimeter; N_2 atmosphere; T_m = melting point; ΔH_f = heat of fusion; T_c = temperature of max. crystallization; ΔH_c = heat of crystallization.

^b Heating rate 10°C/min up to 200°C.

^c Cooling rate 5°C/min from 200° to 35°C.

^d Shoulder temperature.

must have been consumed in the initial reaction, but most of the induced reaction must have occurred in the absence of oxygen.¹¹ In the case of ultraviolet exposure, oxygen must have played a significant role in the degradation as it was continuously replenished by the diffusion during the 100 to 150 hr of exposure.

It is not the purpose of this paper to discuss the detailed chemical reaction mechanism that is induced by the various modes of irradiation with or without oxygen, but rather to examine the resulting material and its relation to the observed change in properties. Therefore, further discussion will deal with the latter aspect exclusively.

Electron beam irradiation produces a high content of insolubles (cross-linking) with little change in crystallinity (see Table II), while ultraviolet irradiation resulted in much chain scission with subsequent secondary crystallization which increases the crystallinity index from 45% to 70%. The chain scission in that case lowered the solution viscosity without the formation of insolubles.⁹

While embrittlement in the case of ultraviolet irradiation appears to be caused by chain scission resulting in increased crystallinity and loss of tie molecules between the crystalline regions,⁹ the electron beam irradiation must produce the same effect by a different mechanism. It is proposed that this mechanism involves a suppression of the plastic flow through the crosslinking of the amorphous phase, i.e., preventing a slippage of chains from the crystallites and rotation of the latter within the spherulitic structure, so that chain scission of the carbon backbone becomes the predominant failure mechanism upon mechanical loading of the crosslinked sample.¹² The explanation seems particularly valid if the crosslinking is preferentially formed in a block-type arrangement, as indicated by the DSC measurements discussed in a later paragraph.

The ultimate tensile strength and elongation data, summarized in Table I and shown graphically in Figures 1 and 2, indicate that these properties decrease with increasing irradiation dosage, both at ambient and elevated temperatures. Quite drastic reductions in the strength and elongation characteristics are encountered after exposure to dosages of 5–15 Mrads. Irradiation dosages in excess of 20 Mrads result in further, albeit more moderate, strength and elongation losses. Both the ambient and the elevated tensile strength and elongation values of the unirradiated (control) specimens are superior to those of all the irradiated samples. As shown in Table I, the test data indicate an increase in the yield stress with increasing dosage of irradiation, in particular the yield stress at 100°C, increasing from 1350 to 2000 psi. This phenomenon might be attributed to an increase of the thermal stability of the crystallites at intermediate temperatures below their thermodynamic melting point, due to the cross-linking of the adjacent amorphous phase. Similar observations have been recorded in oriented fibers¹³ and appear to be connected with hindered segmental motion of the chains, resulting in delayed pre-melting of the smaller, less perfect crystallites.

The DSC measurements did not show any indication of an exothermic peak near the melting point due to decay of radicals trapped in the crystallites.¹⁴ This was to be expected since the samples were stored before testing for over two weeks at ambient temperatures. During the first heating cycle, the slight increase in the heat of fusion (ΔH_f , Table II) indicates that the irradiated samples did not undergo a secondary crystallization to any significant extent—even after exposure to 60-Mrad doses. Since the unirradiated samples exhibited low crystallinity, such secondary crystallization would be expected for a linear polymer, given the occurrence of sufficient chain scission upon irradiation. Broad-angle x-ray measurements confirmed the DSC results as they showed a crystallinity index of 51% for the 60-Mrad sample as against 45.5% for the unirradiated control. Also, no abnormal deviations from this trend were noted for the samples with the lower irradiation dosages.

It is noteworthy that subsequent cooling and reheating of the irradiated samples, following the initial heating to 200°C in the DSC unit under nitrogen, did indicate a gradual broadening of the crystallization and melting characteristics with increasing irradiation dosages. Comparing samples with equal thermal history, the maximum observed melting point depression amounted to 6°C (Table II). This melting point depression must be a consequence of branch points introduced by the crosslinking reaction. It is progressive with increasing irradiation dosages up to 30 Mrads, after which it appears to level off with additional dosages. However, the percent of insolubles continues to increase from 80% to 91% with increasing irradiation dosages (Table II).

When calculated by the copolymer equation for melting point depression, the latter equals about 8–10 mole-% branch points. The observation that, once melted, irradiated samples recrystallized upon cooling to approximately the same degree of crystallinity, as is suggested by the heat of fusion (Table II), is an important one when it is compared to a control having the same thermal history. This phenomenon may be explained by the preferential formation of branch points via a block-type arrangement in the amorphous phase, rather than by random placement as is postulated in free radical homo- and copolymerization or crosslinking in the melt. Bohm¹⁵ has shown that post-irradiation reactions include a migration of allyl free radicals from the crystalline regions to the amorphous phase where they will react subsequently with the oxygen diffusing into the polymer to form both stable and unstable oxygen-containing crosslinks. It was observed that the 50- and 60-Mrad samples showed some discoloration. Furthermore, they exhibited a lower degree of thermal stability than the controls as measured by thermogravimetric analysis.

CONCLUSIONS

Solid-state crosslinking of an ultrahigh molecular weight polyethylene resin with high energy electrons in the presence of air results in the deteriora-

tion rather than the improvement of the short-term tensile properties. Furthermore, the properties deteriorate progressively with increasing dosage. A failure mechanism has been suggested for the observed embrittlement which is different from the embrittlement caused by prolonged exposure to ultraviolet irradiation.

The authors wish to express their gratitude to Allied Chemical Corporation for permission to publish this paper, and they are indebted to Mr. E. K. Walsh, Dr. R. J. Fredricks, Mr. R. G. Dell, and Mr. K. J. Tiger from the Chemical Physics Section of Allied Chemical Corporation, Corporate Chemical Research Laboratory, for their dilute solution, x-ray, and thermoanalytical measurements.

References

1. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962, p. 385.
2. R. A. Raff and K. W. Doak, Eds., *Crystalline Olefin Polymers*, Vol. II, Interscience, New York, 1964, p 301.
3. E. M. Fettes, Ed., *Chemical Reactions of Polymers*, Interscience, New York, 1964, p. 726.
4. V. L. Lanza, *Mod. Plastics*, **34**, (11), 129 (1957).
5. B. G. Harper, *J. Appl. Polym. Sci.*, **2**, 363 (1959).
6. Allied Chemical Corporation, Technical Literature.
7. Hercules, Inc., Wilmington, Del., Technical Literature on "Hifax 1900," 1966.
8. Francis, Cook, and Elliot, *J. Polym. Sci.*, **31**, 453 (1958).
9. E. Turi, L. G. Roldan, F. Rahl, and H. J. Oswald, *ACS Polymer Preprints*, **5**, No. 2, 558 (1964).
10. F. M. Winslow and W. L. Hawkins, *High Polymers*, Vol. XX, Part I, Interscience, New York, 1965, page 841.
11. J. H. Bowen and D. V. Rosato, *Environmental Effects on Polymeric Materials*, Vol. I, page 620.
12. S. N. Zhurkov and E. E. Tomashevsky, *Proc. Inst. Physics and Physical Society, Oxford Conference*, Sept. 1966, The Institute of Physics and the Physical Society London(England), 1966, p. 200.
13. D. C. Prevorsek and A. V. Tobolsky, *Text. Res. J.*, 795 (1963).
14. G. G. A. Bohm, J. A. Currie, and Malcolm Dole, *ACS Polymer Preprints*, Vol. 9, No. 1, 303 (1968).
15. G. G. A. Bohm, *J. Polym. Sci. A-2*, **5**, 639 (1967).

Received March 11, 1969

Revised August 18, 1969