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The Effects of Small Doses of Radiation on the Flow and Other Properties of Ziegler Polyethylenes

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Synopsis

We have studied the effects of high energy radiation in doses of up to 1.0 Mrad on the properties of polyethylene. The interactions of some radiation variables and polymer variables have also been determined. The results obtained show that the main effects of radiation on polyethylene are to reduce its melt index and concomitantly to increase its flow parameter. The extent of these changes depends on several other factors. It is reduced by many common antioxidants (with the apparent exception of *N*-stearoyl-*p*-aminophenol). Under the conditions of our experiments it is not affected by the presence of air during irradiation, but it is reduced by post-irradiation milling. Our data also indicate that it increases with decreasing polymer melt index and with decreasing polymer density, but these apparent effects may be artifacts due to variations of antioxidant content. Radiation in small doses has little effect on any of the other properties of polyethylene, including high shear flow properties, softening point, tensile properties, impact strength, folding endurance, stress cracking resistance, thermal stability, and light stability.

INTRODUCTION

When thermoplastics are extruded they are subject to two apparently contradictory demands. They are required to flow easily when passing through the extruder die and they are required to flow with great difficulty after emerging from the die. If they do not flow easily through the die, then the process will be too slow or too power-consuming. If they flow too easily after passing through the die then the extrudate will not be able to carry its own weight and the process will fail by excessive drawdown or even fracture of the extrudate. These demands are not in direct conflict, however, since the shear stresses in the two places are different. They are high in the die and low after the die. For purposes of extrusion, therefore, one requires a polymer which has a relatively low viscosity at high shear stress and a relatively high viscosity at low shear stress. In other words, one requires a polymer having a low melt index and a high flow parameter $[d(\log \text{shear rate})/d(\log \text{shear stress})]$.

One way of increasing the flow parameter of polyethylene is to introduce some long-chain branching or crosslinking. It is well known that poly-

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ethylene can be crosslinked by means of ionizing radiation or chemical additives. Previously we have shown that the main effects of small doses of electron radiation are to decrease the polymer melt index and to increase its stress cracking resistance.[1] We have now studied the effects of high energy radiation on the flow properties of Ziegler polyethylene. In this work we used spent nuclear fuel rods as source of radiation and we applied only very small doses, in the range 0 to 1 Mrad. At the same time we studied the concomitant changes in physical and aging properties of the polymer, thus extending our previous studies of these properties to lower dose levels.

EXPERIMENTAL

We made arrangements with Wantage Radiation Laboratory to have samples of polyethylene irradiated by spent nuclear fuel rods in the Harwell radiation pond. Dose levels applied varied from 0 to 1 Mrad.

All irradiated materials were subjected to a heat treatment (83°C. for 24 hr.) before evaluation in order to terminate any free radicals. Such radicals have been shown by Lawton and co-workers to survive for considerable periods at room temperature, during which time they can cause the polymer to oxidize and become brittle.[2]

We evaluated the flow properties, physical properties, thermal stability, and light stability of the irradiated products.

Our studies also included investigations into the interactions of irradiation with other process variables, including the effect of oxygen during irradiation, the effect of milling after irradiation, the effect of methyl side branching in the polyethylene (ethylene–propylene copolymer), the effect of melt index of the original polymer, and the effects of miscellaneous additives.

In order to exclude oxygen in cases where this was necessary we proceeded as follows. We placed the sample of polyethylene in a polyethylene bag with a sealable opening. We heated the bag and contents in a vacuum oven (100°C. for 12 hr.), repressured to atmospheric pressure with nitrogen, and sealed it. Then we inserted the bag into a second polyethylene bag, sealed the outer bag except for a small vent, flushed it several times with nitrogen and sealed it completely. With such an arrangement we expected that little or no oxygen could contact the polyethylene sample during radiation.

We studied the flow properties of the product in a melt index apparatus. Properties determined included the melt index with the use of the standard 2.16 kg. load and with a 21.6 kg. load, as described previously by van der Vegt and Wilson.[3] From these properties we determined an estimate of the shear sensitivity of the polymer, which we have called the melt indexer flow parameter n, where

$$n = \log \text{MI (21.6 kg. load)} - \log \text{MI (2.16 kg. load)}$$

We also studied the flow properties of some of the products in the gas-driven high-pressure capillary viscometer. Using this apparatus we deter-

mined the maximum shear stress and the maximum shear rate compatible with smooth flow at 200°C., and the viscosity at various temperatures under an applied apparent shear stress of 8.6×10^5 dynes/cm.^{2}.

RESULTS AND DISCUSSION

Influence of High Energy Radiation on the Melt Indexer Flow Properties

We employed a factorial experiment to investigate the effect on flow properties of radiation dose, melt index of polymer, type of polymer, atmosphere during irradiation, and post-irradiation milling. Milling, when applied, involved 10 min. in a Brabender Plastograph at 170°C. in the presence of additional Santonox (0.02 phr).

The results obtained are listed in Tables I and II. A typical cross-section of the data—those representing polymers which were irradiated in air and then milled—are analyzed graphically in Figures 1 and 2. It will be

TABLE I
Influence of High Energy Radiation on Flow Properties of Polyethylene

Polymer	Radiation atmosphere	Radiation dose, Mrad	Melt index, g./10 min. 2.16 kg. load	Melt index, g./10 min. 21.6 kg. load	Melt indexer flow parameter n
A	—	0.0	1.87	70	1.57
Homopolyethylene, d	Air	0.2	1.61	72	1.65
= 0.959 g./cc., San-	Air	0.4	1.24	66	1.73
tonox 0.01 phr	Air	1.0	0.41	39	1.98
	N_2	0.2	1.50	69	1.66
	N_2	0.4	1.17	65	1.75
	N_2	1.0	0.29	33	2.06
B	—	0.0	0.69	27	1.59
Homopolyethylene, d	Air	0.2	0.47	24	1.71
= 0.957 g./cc., San-	Air	0.4	0.27	20	1.87
tonox 0.02 phr	Air	1.0	0.028	6.3	2.35
	N_2	0.2	0.45	22	1.69
	N_2	0.4	0.26	17.5	1.83
	N_2	1.0	0.036	8.2	2.36
C	—	0.0	1.80	58	1.51
Ethylene–propylene co-	Air	0.2	1.47	56	1.58
polymer, d = 0.951	Air	0.4	0.95	47	1.69
g./cc., Santonox 0.01	Air	1.0	0.106	16.4	2.19
phr	N_2	0.2	1.36	53	1.59
	N_2	0.4	0.97	47	1.69
	N_2	1.0	0.19	18.6	1.99
D	—	0.0	0.40	13.4	1.53
Ethylene–propylene co-	Air	0.2	0.22	10.6	1.68
polymer, d = 0.949	Air	0.4	0.116	7.6	1.82
g./cc., Santonox 0.01	Air	1.0	0.0071	2.2	2.49
phr	N_2	0.2	0.23	10.2	1.65
	N_2	0.4	0.094	7.2	1.88
	N_2	1.0	0.006	2.0	2.52

TABLE II
Influence of High Energy Radiation and Milling on Flow Properties of Polyethylene[a]

Polymer[b]	Radiation atmosphere	Radiation dose, Mrad	Melt index, g./10 min. 2.16 kg. load	Melt index, g./10 min. 21.6 kg. load	Melt indexer flow parameter n
A	—	0.0	1.87	70	1.57
	Air	0.2	1.70	74	1.64
	Air	0.4	1.47	72	1.69
	Air	1.0	1.03	69	1.83
	N_2	0.2	1.63	74	1.66
	N_2	0.4	1.42	72	1.71
	N_2	1.0	0.99	70	1.85
B	—	0.0	0.69	27	1.59
	Air	0.2	0.51	26	1.71
	Air	0.4	0.38	24	1.80
	Air	1.0	0.077	13.3	2.24
	N_2	0.2	0.49	25	1.71
	N_2	0.4	0.37	25	1.83
	N_2	1.0	0.115	14.4	2.10
C	—	0.0	1.80	58	1.51
	Air	0.2	1.50	57	1.58
	Air	0.4	1.15	53	1.66
	Air	1.0	0.48	44	1.96
	N_2	0.2	1.49	57	1.58
	N_2	0.4	1.19	52	1.64
	N_2	1.0	0.55	45	1.91
D	—	0.0	0.40	13.4	1.53
	Air	0.2	0.25	12.2	1.69
	Air	0.4	0.156	10.4	1.82
	Air	1.0	0.012	3.7	2.49
	N_2	0.2	0.24	11.9	1.70
	N_2	0.4	0.14	9.5	1.83
	N_2	1.0	0.0082	3.1	2.58

[a] Milling is applied for 10 min. at 170°C. in the presence of 0.02 phr additional Santonox R.

[b] See Table I.

seen that radiation always reduces the melt index of polyethylene and increases its flow parameter. Both changes are quite marked and they take place in concert (see Fig. 3). The extent of the changes brought about also depends upon the other factors involved. Thus, the lower the melt index or the lower the density of the original polymer, then the more marked is the effect of radiation on flow properties. The presence of air during irradiation does not seem to have any very marked effect. This is perhaps surprising, since Matsuo and Dole[4] and Okada and co-workers[5,6] found that oxygen markedly reduces the effects of γ-radiation on polyethylene.

We then analyzed the data in a more quantitative manner, reducing them to two equations. For this purpose we decided to employ only the results which had been obtained on milled samples. Unmilled samples,

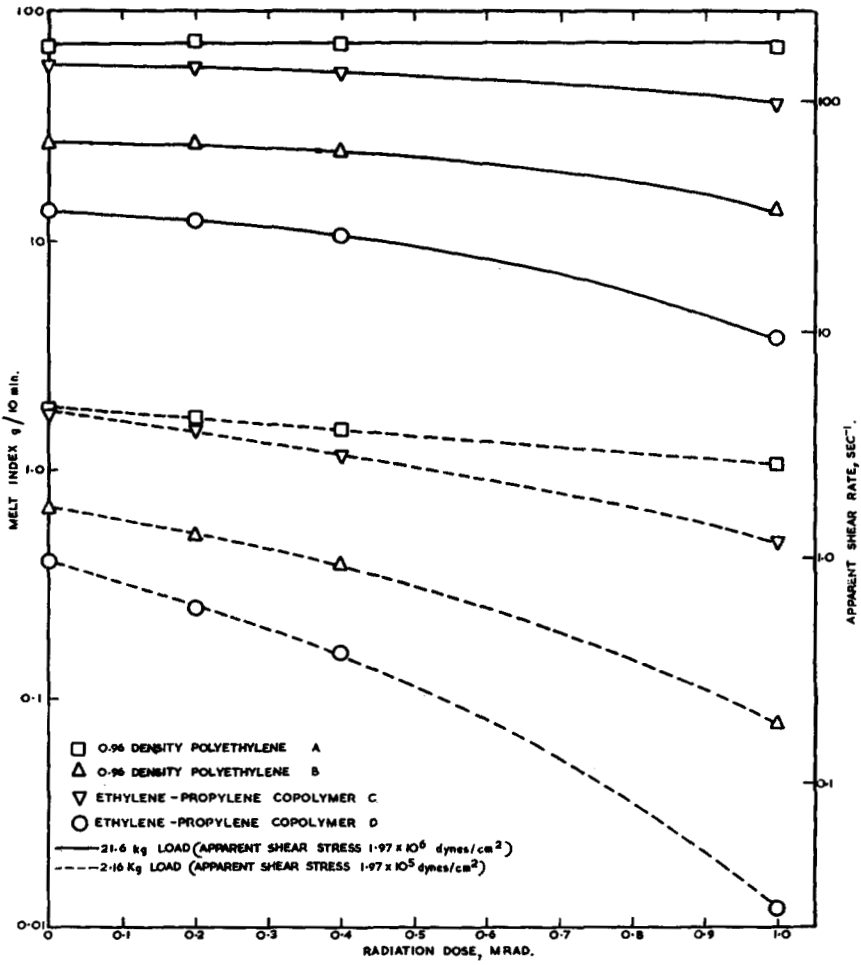

Fig. 1. Influence of high energy radiation on melt index of polyethylenes. (Radiation in air followed by milling.)

it appeared, showed melt indices which increased during measurement. This we considered was probably due to mechanical breakdown of an extensive but tenuous network structure. We preferred to eliminate this cause of variability by employing only results from milled samples. The effects of the radiation on the flow properties of polyethylenes are summarized fairly well by the very simple relations shown as eqs. (1) and (2).

$$\log \text{M.I.}_D = \log \text{M.I.}_0 - D[0.60 - 1.39 \log \text{M.I.}_0 + 35(0.960 - d)] \quad (1)$$

$$n_D = n_0 + D[0.47 - 0.80 \log \text{M.I.}_0 + 17(0.960 - d)] \quad (2)$$

Here D is the radiation dose in megarad, M.I. is the melt index of the polymer, d is the density of the polymer, and n is the melt indexer flow parameter of the polymer.

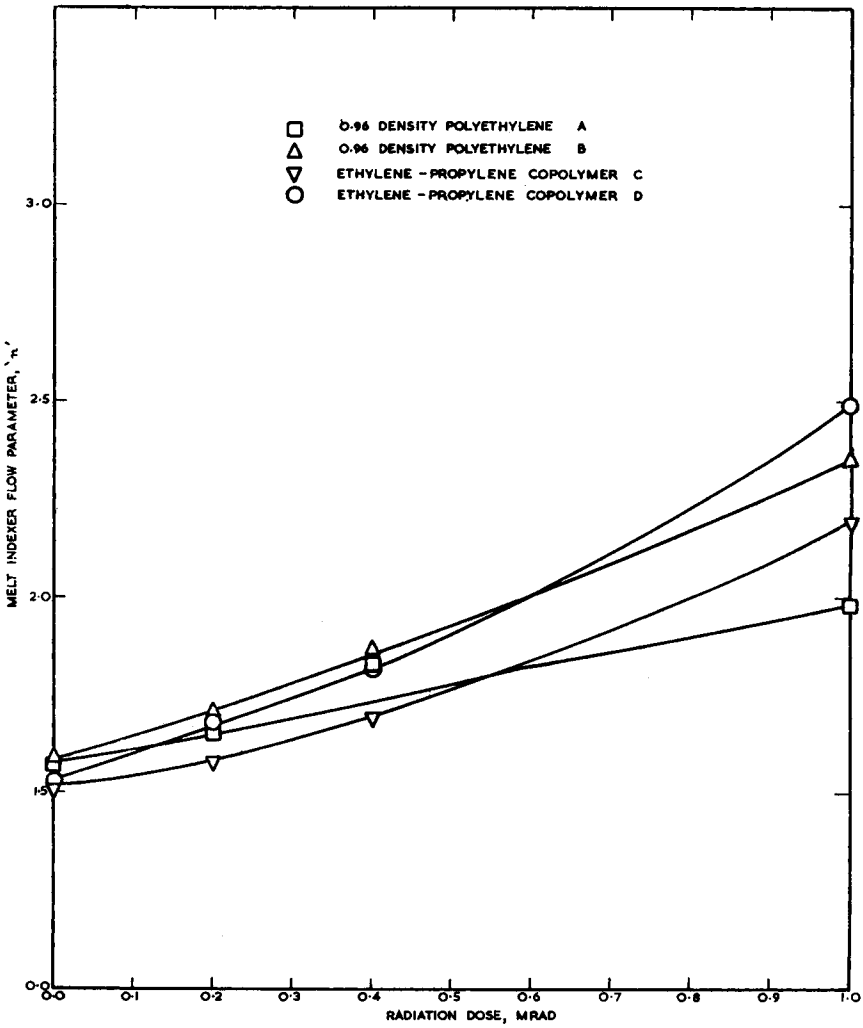

Fig. 2. Influence of high energy radiation on flow parameter of polyethylenes. (Radiation in air followed by milling.)

Alternatively, the experimental data are summarized more accurately by the more complex equations, eqs. (3) and (4).

$$\log \text{M.I.}_D = 0.03 + 0.80 \log \text{M.I.}_0 + 7.6(0.960 - d) - D\,[0.59 - 1.58 \log \text{M.I.}_0 + 48(0.960 - d)] \quad (95\% \text{ confidence limit } \pm 0.16) \tag{3}$$

$$n_D = 1.29 + 0.21n_0 - 15(0.960 - d) + D[-17.75 + 11.33n_0 - 130(0.960 - d)] \quad (95\% \text{ confidence limit } \pm 0.16) \tag{4}$$

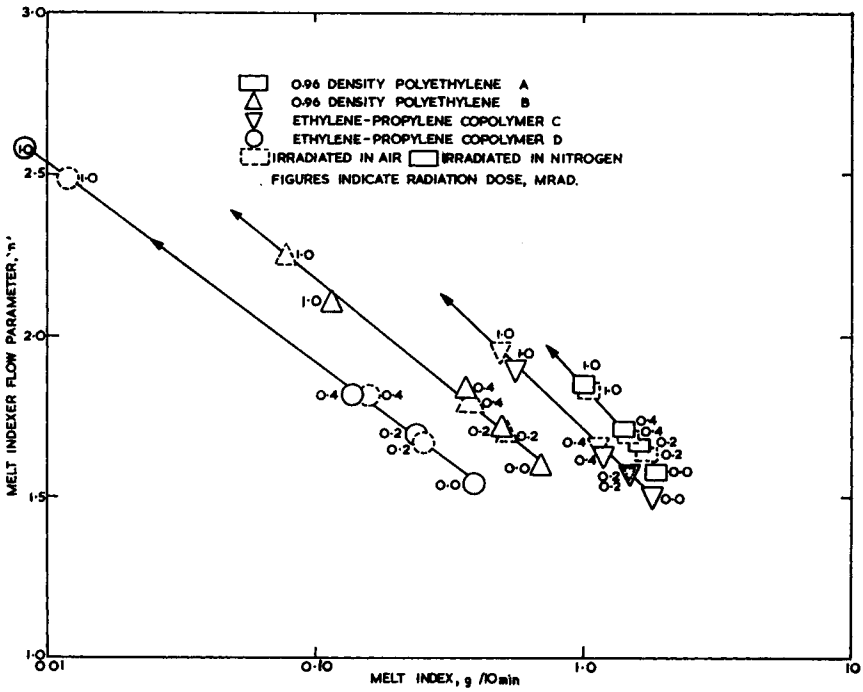

Fig. 3. Joint changes in melt index and flow parameter of polyethylenes caused by high energy radiation and milling.

Although these equations represent the present data fairly accurately, it is not known how far they apply to other polyethylenes having melt indices or densities outside the range considered. Indeed, it must be stated that these findings contradict to some extent the conclusions of our earlier probing experiments. Here we showed, for example, that the radiation sensitivity of polyethylene increases with increasing, not decreasing, density.[1] The cause of these apparent contradictions has not been positively identified, but it is probably due to variations in stabilization. As will be shown below, the radiation sensitivity of polyethylene depends strongly on the presence of antioxidants, and especially on the presence of 4,4′-thiobis(3-methyl-6-*tert*-butyl phenol) (Santonox R). Small accidental differences in Santonox R content would have an appreciable effect. It may, therefore, be that the effects we have attributed to melt index and density of the polymer are artifacts caused by variations of Santonox R content.

Influence of Additives on the Effects of High Energy Radiation

Many different types of chemical compounds are likely to be present in trace amounts in Ziegler polyethylene. These include catalyst remnants, stabilizers, and other additives. Statements occur in the literature to the effect that antioxidants (especially Santonox R[7]) reduce the G value of

TABLE III
Influence of Additives and High Energy Radiation on Flow Properties of Polyethylene (Ethylene–Propylene Copolymer E)

Additive		Radiation, dose, Mrad	Melt index, g./10 min.		Melt indexer flow parameter n
Type	Concentration, phr		2.16 kg. load	21.6 kg. load	
None	0.0	0.00	1.04	31	1.47
2,2′-Methylene bis(4-methyl-6-*tert*-butyl phenol)	0.1	0.93	0.41	23	1.75
2,6-Di-*tert*-butyl-*p*-cresol	0.1	0.93	0.40	21	1.72
Tris(nonylphenyl) phosphite	0.1	0.93	0.39	19.9	1.71
Tris(laurylthio) phosphite	0.1	0.93	0.31	18.5	1.78
4,4′-Thiobis(3-methyl-6-*tert*-butyl phenol)	0.1	0.93	0.26	17.0	1.82
Ionox 330 (phenolic antioxidant)	0.1	0.93	0.26	17.6	1.83
Dilauryl thiodipropionate	0.1	0.93	0.23	18.6	1.91
2-Hydroxy-4-*n*-octoxybenzophenone	0.1	0.93	0.16	11.7	1.86
N,N′-Di-β-naphthyl-*p*-phenylenediamine	0.1	0.93	0.16	12.1	1.88
Octylphenyl salicylate	0.1	0.93	0.14	13.1	1.98
Trilauryl phosphite	0.1	0.93	0.13	9.9	1.88
Calcium stearate	0.2	0.93	0.067	10.3	2.19
N-Stearoyl-*p*-aminophenol	0.1	0.93	0.049	6.7	2.14
None	0.0	0.93	0.038	7.2	2.28
Aluminium oxide	0.2	0.93	0.031	7.3	2.24
Titanium dioxide (rutile)	0.2	0.93	0.019	5.8	2.49

radiation by trapping radicals. Claims have been made that some antioxidants (especially *N*,*N'*-di-β-naphthyl-*p*-phenylenediamine[8,9]) have less inhibiting effect than others. On the other hand, claims have been made for various compounds which increase the *G* value of radiation, for example, zinc diethyl dithiocarbamate,[10] divinyl aromatic hydrocarbons,[11] chlorobenzene,[12] and polyfunctional monomers such as allyl acrylate.[13] Clearly, we had to investigate the effects of any compound which is likely to be present in Ziegler polyethylene.

We therefore prepared a series of samples of polyethylene, all based upon one polymer (a propylene-modified polyethylene, reference E). Each sample contained an additive, representing a catalyst remnant or a stabilizer. Samples were irradiated by spent nuclear fuel rods in the Harwell radiation pond, receiving a dose of 0.93 Mrad at a rate of 1.76 Mrad/hr. The flow properties of the resulting products are shown in Table III, where they are listed in order of diminishing melt index.

The results show that most antioxidants and light stabilizers strongly reduce the effect of radiation on the flow properties of polyethylene. In terms of changes in log (melt index) or flow parameter, 0.1 phr of antioxidant generally reduces the effect of radiation by about 60%. This is a very significant effect and would certainly have to be taken into account in any commercial application of radiation to polyethylene.

There is, however, one apparent exception. *N*-Stearoyl-*p*-aminophenol appears to have little effect on the radiation sensitivity of the polymer. It would, therefore, be an excellent antioxidant to choose for polyethylene if an irradiation step is subsequently to be applied.

Catalyst residues have relatively little effect. At the concentrations which normally occur in Ziegler polyethylene their effects on the radiation sensitivity of the polymer can safely be ignored.

Influence of High Energy Radiation on the High Shear Flow of Polyethylene

We studied the high shear flow properties of the irradiated polyethylene samples using a high-pressure nitrogen-driven capillary viscometer (capillary length 10 mm., diameter 0.5 mm.) at 200°C. The flow curves of one of the polymers examined, before and after various doses of radiation, appear in Figure 4. It will be seen that the polymers with radiation doses of 0.0, 0.2, and 0.4 Mrad have flow curves which are virtually identical. The polymer with a radiation dose of 1 Mrad also shows identical flow behavior at high shear stress and slightly (barely significantly) less flow at lower shear stress. It will also be seen that the critical flow conditions, which cause the extrudate to emerge rough instead of smooth, are likewise unaffected by radiation.

Similar results were obtained in the case of the other polymers examined The data for their critical shear conditions are summarized in Table IV. One may safely conclude, therefore, that the high shear flow of polyethylene is virtually unaffected by high energy radiation in doses of up to 1 Mrad.

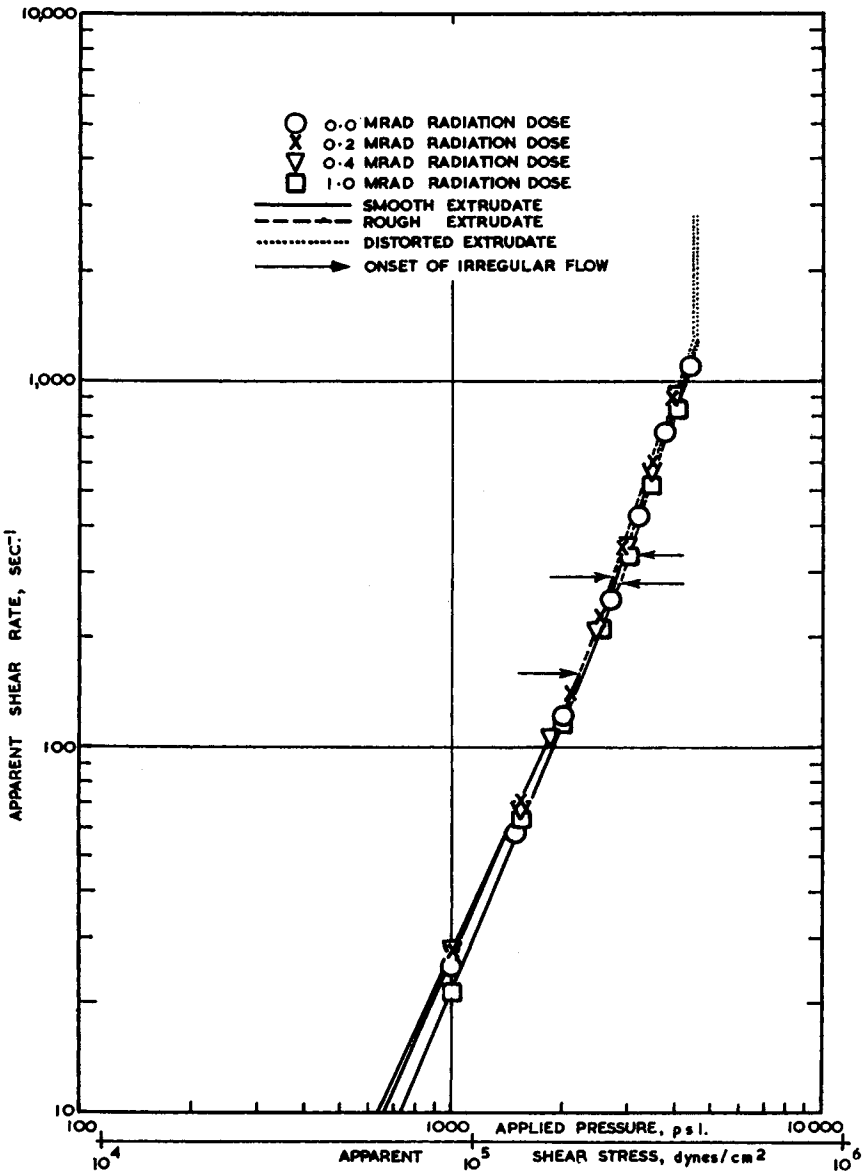

Fig. 4. Influence of high energy radiation on the high shear flow of polyethylene at 200°C. (ethylene–propylene copolymer E).

This conclusion stands in marked contrast to the extensive falls in low shear flow, as evidenced by melt index, which are caused by the same doses of radiation.

Using the high-pressure capillary viscometer, we also determined the flow of each polymer under a standard applied pressure of 1000 psi (apparent shear stress 8.6×10^5 dyne/cm.^{2}) at four temperatures: 150, 200, 250, and

TABLE IV
Influence of High Energy Radiation on Critical Flow Properties of Polyethylenes at 200°C.

Polymer	Radiation dose, Rrad	Melt index, g./10 min.	Max. shear stress compatible with smooth flow × 10^{-6}, dynes/cm.^{2}	Max. shear rate compatible with smooth flow, sec.$^{-1}$
A	0.0	1.87	>3.4	>4800
	0.2	1.70	2.4	1600
	0.4	1.47	2.7	1800
	1.0	1.03	2.7	2750
B	0.0	0.69	2.0	460
	0.2	0.51	2.0	390
	0.4	0.38	2.0	370
	1.0	0.077	2.4	660
C	0.0	1.80	2.4	1250
	0.2	1.50	2.4	1150
	0.4	1.15	2.4	1250
	1.0	0.48	2.8	1850
D	0.0	0.40	2.5	340
	0.2	0.25	2.3	280
	0.4	0.156	1.9	160
	1.0	0.012	2.4	280

[a] See Table I.

TABLE V
Influence of High Energy Radiation on the Temperature Sensitivity of High Shear Viscosity of Polyethylene

Polymer[a]	Radiation dose, Mrad	E_{vis}, kcal./mole
A	0.0	7.3
	0.2	7.1
	0.4	7.7
	1.0	7.4
B	0.0	7.1
	0.2	7.2
	0.4	7.0
	1.0	8.1
C	0.0	6.7
	0.2	7.2
	0.4	7.2
	1.0	7.1
D	0.0	7.5
	0.2	7.4
	0.4	7.8
	1.0	8.2

[a] See Table I.

300°C. From these experiments we derived the activation energies of viscous flow (E_{vis}) shown in Table V. It will be seen that high energy radiation in the doses applied causes a slight but not statistically significant

TABLE VI
Influence of High Energy Radiation and Milling on Physical Properties of Polyethylene[a]

		Physical properties								
Polymer[b]	Radiation dose, Mrad	Melt index, g./10 min.	Vicat softening point, °C.	Density, g./cc.	Tensile yield stress, psi	Tensile ultimate stress, psi	Tensile ultimate elongation, %	Folding endurance (Köhler-Molin) no. of flexures to break	Izod impact strength, ft.-lb./in. notch	Environmental stress cracking resistance, F_{50} hr. (in Igepal)
A	0.0	1.87	127	0.959	4520	3540	950	800	2.8	<10
	0.2	1.70	129	0.960	4470	3890	950	850	2.2	<10
	0.4	1.47	130	0.960	4610	3490	630	850	2.8	<10
	1.0	1.03	129	0.961	4790	2830	280	1100	3.6	<10
B	0.0	0.69	131	0.957	4490	5170	870	1750	6.8	35
	0.2	0.51	133	0.957	4420	5170	860	1850	5.8	36
	0.4	0.38	133	0.958	4590	4840	860	1600	6.9	41
	1.0	0.077	136	0.960	5040	2940	540	1050	7.2	60
C	0.0	1.80	126	0.951	3810	5480	1100	900	2.5	29
	0.2	1.50	126	0.950	3870	4010	950	900	2.8	29
	0.4	1.15	126	0.950	3800	4770	1000	900	2.6	26
	1.0	0.48	126	0.951	3850	4120	920	900	3.3	22
D	0.0	0.40	131	0.949	3730	6090	920	2600	7.0	100
	0.2	0.25	128	0.948	3730	5880	820	2500	6.8	145
	0.4	0.156	128	0.949	3830	6320	820	2500	7.2	175
	1.0	0.012	129	0.949	4090	3380	460	2450	6.8	125

[a] Radiation is applied to the polymers in air. Milling is applied for 10 min. at 170°C. in presence of 0.02 phr additional Santonox R.
[b] See Table I.

increase in E_{vis}. An increase would be in line with the conclusions of Tung that the E_{vis} of polyethylene increases with increasing degree of long-chain branching.[14] In the case of our results, however, the effect is probably small enough to be ignored.

Influence of High Energy Radiation on Physical Properties of Polyethylene

The physical properties of the irradiated polyethylenes prepared as described above are shown in Table VI.

The results obtained show that all of the physical properties examined are substantially unaffected by radiation in doses of up to 1 Mrad. Density and yield strength increase slightly. Ultimate tensile stress and elongation fall slightly. No significant changes occur in softening point, folding endurance, impact strength, or environmental stress cracking resistance. The charges that do occur are all quite small in relation to the accompanying reduction in melt index. This is remarkable in the cases of impact strength and environmental stress cracking resistance, both of which normally increase steeply as melt index is reduced. The small changes in physical properties may, however, be regarded as more normal when they are studied in relation to the changes in the 21.6 kg. melt index, which is hardly affected by small doses of radiation.

TABLE VII
Influence of High Energy Radiation and Milling on the Aging of Polyethylenes[a]

Polymer[b]	Santonox R content, phr: Added before irradiation	Santonox R content, phr: Added before milling	Radiation dose, Mrad	Thermal stability (oven life at 120°C.), hr.[c]	Light stability (Xeno-test life), hr.
A	0.01	0.02	0.0	>1100 (170%)	210
			0.2	>1100 (165%)	180
			0.4	>1100 (165%)	170
			1.0	>1100 (110%)	190
B	0.02	0.02	0.0	>1100 (135%)	360
			0.2	>1100 (170%)	200
			0.4	>1100 (145%)	160
			1.0	>1100 (150%)	150
C	0.01	0.02	0.0	840	—
			0.2	840	—
			0.4	1100	—
			1.0	1100	—
D	0.01	0.02	0.0	640	—
			0.2	640	—
			0.4	840	—
			1.0	840	—

[a] Radiation is applied to the polymers in air. Milling is applied for 10 min. at 170°C.
[b] See Table I.
[c] Figures in parentheses represent folding endurance (Köhler-Molin) after 1100 hr. in oven, as a percentage of original folding endurance.

Influence of High Energy Radiation on Aging Properties of Polyethylene

The thermal stabilities and the light stabilities of irradiated polyethylenes, prepared as described above, are shown in Table VII.

Thermal stability is determined as the length of time in an oven at 120°C. which is required to make the polymer brittle. The figures show that radiation has no adverse effect on the thermal stability of polyethylene. It must, however, be noted that all the samples examined had been milled after irradiation and before test, and that an appreciable amount of antioxidant (Santonox R, 0.02 phr) had been added to safeguard the polymer during milling. Other conditions of test need not necessarily give the same result.

Light stability is determined as the length of time in a Xenotest apparatus which is required to make the polymer brittle. The results obtained show that radiation diminishes the light stability of polyethylenes in the two cases examined. The damage is only slight in one case but it is appreciable in the other.

CONCLUSIONS

The most promising applications for small doses of high energy radiation in polyethylene technology are in the manufacture of grades having an unusually low melt index in comparison with the other properties of the polymer. This can be a desirable feature of extrusion and vacuum forming grades generally, where the demand for sufficient melt strength can sometimes force one to employ a lower melt index than would otherwise be necessary.

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References

1. Wright, B., *J. Appl. Polymer Sci.*, **7**, 1905 (1963).
2. Lawton, E. J., R. S. Powell, and J. S. Balwit, *J. Polymer Sci.*, **32**, 257, 277 (1958); E. J. Lawton, J. S. Balwit, and R. S. Powell, *J. Chem. Phys.*, **33**, 395, 405 (1960).
3. van der Vegt, A. K., and W. R. K. Wilson, *Soc. Chem. Ind. Monograph*, **17**, 108 (1963).
4. Matsuo, H., and M. Dole, *J. Phys. Chem.*, **63**, 837 (1959).
5. Okada, Y., *J. Appl. Polymer Sci.*, **7**, 695, 703 (1963).
6. Okada, Y., and A. Amemiya, *J. Polymer Sci.*, **50**, 822 (1961).
7. Althouse, V. E., paper presented to the Division of Polymer Chemistry, 144th American Chemical Society Meeting, Los Angeles, April 1963; *Preprints*, **4**, No. 1, 256 (1963).
8. General Electric Company, Brit. Pat. 830,899 (1960) claiming 16.5.55 (U.S.A.).
9. T. I. (Group Services) Ltd., Brit. Pat., 853,737 (1960), claiming 9.5.57.
10. Sequoia Process Corp., Belg. Pat. 555,720 (1957), claiming 15.3.56 (U.S.A.).
11. Esso Res. and Engng. Co., Fr. Pat. 1,205,200 (1960) claiming 24.10.57 (U.S.A.).
12. General Electric Co., Brit. Pat. 849,042 (1960) claiming 20.5.57. (U.S.A.).

13. Odian, G., and B. S. Bernstein, paper presented to the Division of Polymer Chemistry, 142nd American Chemical Society Meeting, Atlantic City, September 1962; *Preprints*, **3**, No. 2, 221 (1962).

14. Tung, L. H., *J. Polymer Sci.*, **43**, 409 (1960).

Résumé

Nous avons étudié l'influence des radiations d'énergie élevée à des doses allant jusqu'à 1.0 Mrad sur les propriétés du polyéthylène. On a également déterminé les interactions de certaines variables propres aux radiations et de certaines variables propres au poly mere. Les résultats obtenus montrent que l'influence principale de la radiation sur le polyéthylène est de réduire son indice de fusion et d'augmenter en même temps son paramètre d'écoulement. L'importance de ces changements dépend de plusieurs autres facteurs. Elle est réduite au moyen de plusieurs antioxydants habituels (à l'exception du *N*-stéaroyl-*p*-aminophénol). Dans nos conditions expérimentales, elle n'est pas influencée par la présence d'air pendant l'irradiation, mais elle est réduite par mélange après irradiation. Nos résultats montrent également que l'importance de ces modifications augmente avec la diminution de l'indice de fusion et avec la diminution de la densité du polymère, mais ces effets apparents doivent etre des artefacts dûs aux variations de la teneur en antioxydant. La radiation à faibles doses a une légère influence sur chacune des autres propriétes du polyéthylène tels que les propriétés d'écoulement a cisaillement élevé, le point de ramollissement, les propriétés de tension, la force d'impact, la résistance au pliage, la résistance a la force de rupture, la stabilité thermique et la stabilité à la lumière.

Zusammenfassung

Der Einfluss hochenergetischer Strahlung in Dosen bis zu 1,0 Mrad auf die Eigenschaften von Polyäthylen wurde untersucht. Die Beziehung zwischen einigen Strahlungsvariablen und Polymervariablen wurde bestimmt. Die erhaltenen Ergebnisse zeigen, dass der Haupteinfluss der Strahlung auf Polyäthylen in einer Herabsetzung seines Schmelzindex und einer gleichzeitigen Erhöhung seines Fliessparameters besteht. Das Ausmass dieser Änderungen hängt von einigen anderen Faktoren ab. Es wird durch viele übliche Antioxidantien (mit der offenbaren Ausnahme von *N*-Stearoyl-*p*-aminophenol) herabgesetzt. Unter den angewendeten Versuchsbedingungen wird es durch Anwesenheit von Luft während der Bestrahlung nicht beeinflusst, hingegen durch Bearbeitung nach der Bestrahlung herabgesetzt. Die Daten zeigen auch, dass es mit abnehmendem Schmelzindex des Polymeren und mit fallender Polymerdichte zunimmt, jedoch können diese scheinbaren Effekte auf der Anderung des Antioxidantsgehalts beruhende Artefakte sein. Strahlung in kleinen Dosen hat wenig Einfluss auf irgendeine andere Eigenschaft vonPolyäthylen, einschliesslich der Fliesseigenschaften bei hoher Scherung, des Erweichungspunkts, der Spannungseigenschaften, der Stossfestigkeit, der Faltungsbeständigkeit, der Beständigket gegen Spannungsrissbildung, der thermischen Stabilität und der Lichtstabilität.

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