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The Effects of Electron Radiation on the Properties of Ziegler Polyethylenes

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INTRODUCTION

It is well known that polyethylenes exposed to ionizing radiation of any sort exhibit changes in their physical properties due to crosslinking of the polymer. In many respects the changes induced are desirable—increased resistance to deformation at high temperature, increased resistance to stress cracking, and decreased solubility in solvents.

In previous work the crosslinking effects of radiation have been investigated for high and low density polyethylenes. For example, Lawton et al.[1] showed that crosslinks are formed mainly in the amorphous regions of the polymer. In the case of a high density polyethylene the formation of crosslinks is greatly increased if radiation takes place above the crystal melting point. But, however the crosslinking is carried out, there are substantial changes in polymer properties. These changes are especially notable at higher temperatures when the crosslinked polymer becomes rubberlike and loses its power to flow. From a study and theoretical treatment of the high temperature rubber elasticity of irradiated polyethylenes it is possible to estimate the amount of crosslinkage which has taken place.[2]

Although these and other studies[3,4] have helped to elucidate the mechanism of crosslinkage in polyethylene, the greatest practical interest still attaches to the effect of radiation on the physical properties measured under normal conditions. In this connection a great amount of information is available for low density polyethylenes and much of this work has been summarized by Charlesby.[5] Rather less information is available concerning property changes in high density polyethylene. However, Charlesby[5] reported that Hostalen high density polyethylene gives a reduction in elongation and a slight increase in yield stress when irradiated. Similarly, Waddington[6] has reported on increases in swelling ratio and gel content with several high density polyethylenes.

However, at the present time there is no study of the effects of radiation on the physical properties of different types of high density polyethylenes and we considered that it would be useful to carry out such an investigation. In this work we took care to exclude oxygen and also used a high concentration of antioxidant with a view to eliminating side reactions due to oxidation.

TABLE I
The Effect of Electron Radiation on the Physical Properties of Ziegler Polyethylenes

Polymer	Radiation dose, Mrad	Melt index, g./10 min. (10 kg. load)	Density at 23°C., g./cc.	Softening point, °C.	Tensile properties: Yield stress, psi	Tensile properties: Ultimate stress, psi	Tensile properties: Ultimate elongation, %	Impact strength, ft. lb./in. notch (injection molded bars)	Power factor[a] at 10^6 cycles/sec. tan $\delta \times 10^5$	Flex resistance, Köhler Molin no. of flexes to fracture	Environmental stress cracking resistance, hr. (in Igepal)
1	0	0.25	0.9467	113.0	3470	>4500	>740	11.6	42		287
	2	0.010	0.9467	117.0	3500	>4890	>750	10.8	43		492
	5	<0.001	0.9476	112.5	3670	>4410	>740	9.7	64		378
	10	<0.001	0.9476	116.5	3500	>4390	>680	13.9	74 (→ 80)		>2000
	25	<0.001	0.9476	118.0	3690	3500	360	22.8	62		>2000
	50	<0.001	0.9474	118.5	3640	4290	200	18.7	46		—
	75	<0.001	0.9484	120.0	3670	4550	170	16.5	57		—
2	0	2.6	0.9478	109.0	3710	2170	300	3.3	30	2240	22
	2	0.29	0.9478	108.0	3770	2260	550	3.1	43	744	57
	5	0.015	0.9484	108.0	3710	2250	560	3.3	53	705	495
	10	<0.001	0.9484	112.0	3740	2550	530	3.9	57 (→ 53)	(1090)	>2000
	25	<0.001	0.9478	114.0	3770	2970	260	22.4	48	462	>2000
	50	<0.001	0.9462	115.0	3770	4560	230	18.4	37	19	—
	75	<0.001	0.9487	119.0	3900	4370	200	17.8	49	22	—

3	0	35.0	0.9497	102.0	3790	2000	180	1.3	51	0 (50% broke on bending)
	2	6.7	0.9497	102.5	3660	2000	140	1.4	72	
	5	0.31	0.9501	105.0	3770	2050	130	1.4	86	22
	10	<0.001	0.9501	106.0	3640	2190	130	1.6	89 (→ 96)	334
	25	<0.001	0.9493	111.0	3780	2630	230	6.0	89	>2000
	50	<0.001	0.9489	115.0	3750	3340	170	20.4	77	—
	75	<0.001	0.9489	114.0	3840	4050	270	19.6	71	—
4	0	5.7	0.9528	109.0	4020	>3830	>940	3.8	61	47
	2	0.085	0.9528	113.0	4030	2580	600	3.6	82	—
	5	<0.001	0.9538	115.0	4100	2520	490	3.8	102	> 680
	10	<0.001	0.9538	113.0	4060	2630	470	5.1	107 (→ 96)	>2000
	25	<0.001	0.9534	115.0	4140	3280	160	22.8	87	>2000
	50	<0.001	0.9514	115.0	4000	4670	200	18.6	61	—
	75	<0.001	0.9537	116.0	4230	4710	180	15.6	70	—
5	0	2.2	0.9564	123.0	4090	>4220	>780	—	49	47
	2	0.020	0.9564	124.0	4100	>4030	>750	—	43	—
	5	<0.001	0.9573	122.0	4000	2270	460	—	47	>2000
	10	<0.001	0.9580	—	4350	3900	270	—	63 (→ 68)	—
	25	<0.001	0.9582	—	4310	3940	210	—	54	>2000
	50	<0.001	0.9592	—	4380	4400	160	—	39	—
	75	<0.001	0.9595	127.0	4530	4280	80	—	51	—

[a] The figures in the main column show power factors which were measured within one week of radiation. The figures in parentheses were repeat determinations made two months later.

This project was helped by the use of a source of high energy radiation recently made available in Manchester by Associated Vickers Electrical Co., Ltd. Their source is an Orthotron—a linear accelerator of their own design and manufacture which produces 4 M.e.V. electrons at a rate of 15 μ-amps.

EXPERIMENTAL

Five different high density polyethylenes were used in the electron radiation experiments—three conventional Ziegler polyethylenes of nominal density 0.95 g./cc. having widely different melt indices, and two more highly crystalline Ziegler polyethylenes of medium melt index. The polymers were all blended with antioxidants—trilauryl phosphite (0.3%) and di-β-naphthyl-p-phenylenediamine (0.1%)—to prevent postradiation degradation.

From each polymer seven sets of test pieces were prepared, each set being suitable for the determination of softening point,[7] tensile properties,[8] impact strength,[9] power factor[10] flex resistance and stress cracking resistance.[11] It was proposed also to determine densities and melt indices[12] but special test pieces were not required for these properties. Each set of test pieces was fastened onto a hardboard card with iron wire, placed in a polyethylene bag and purged several times with nitrogen.

The assemblies of test pieces, still blanketed in nitrogen, were mounted on a traversing platform in front of the linear accelerator. They were repeatedly transported through the beam of electrons until they had received the necessary dose. The energy of the electrons employed was 4 M.e.V. and the dose rate was 1 Mrad/min. The radiation doses applied to the seven individual assemblies of test pieces were 0, 2, 5, 10, 25, 50, and 75 Mrad respectively. All test pieces were stored in nitrogen for three days after irradiation to allow decay of the free radicals. They were then tested by the appropriate methods. The data obtained are listed in Table I.

RESULTS

Melt Index

An immediate and drastic reduction of melt index (10 kg. load) occurs at quite small radiation doses (see Fig. 1). No flow is observed with any of the polymers examined after a dose of 10 Mrad or more. The maximum dose which can be applied to any of these polyethylenes, if they are subsequently to be extruded or injection molded, would appear to be about 5 Mrad.

By plotting the results as a graph of log (melt index) versus radiation dose, as in Figure 1, it becomes evident that the behavior of each polymer can be represented approximately by a straight line. The slope of the line may be used to characterize the radiation sensitivity of the polymer.

The slopes obtained for the five polymers examined, together with their original melt indices and densities, are shown in Table II.

From these results it will be seen that radiation sensitivity increases markedly with increasing polymer density, and that it also increases somewhat with decreasing melt index (increasing molecular weight).

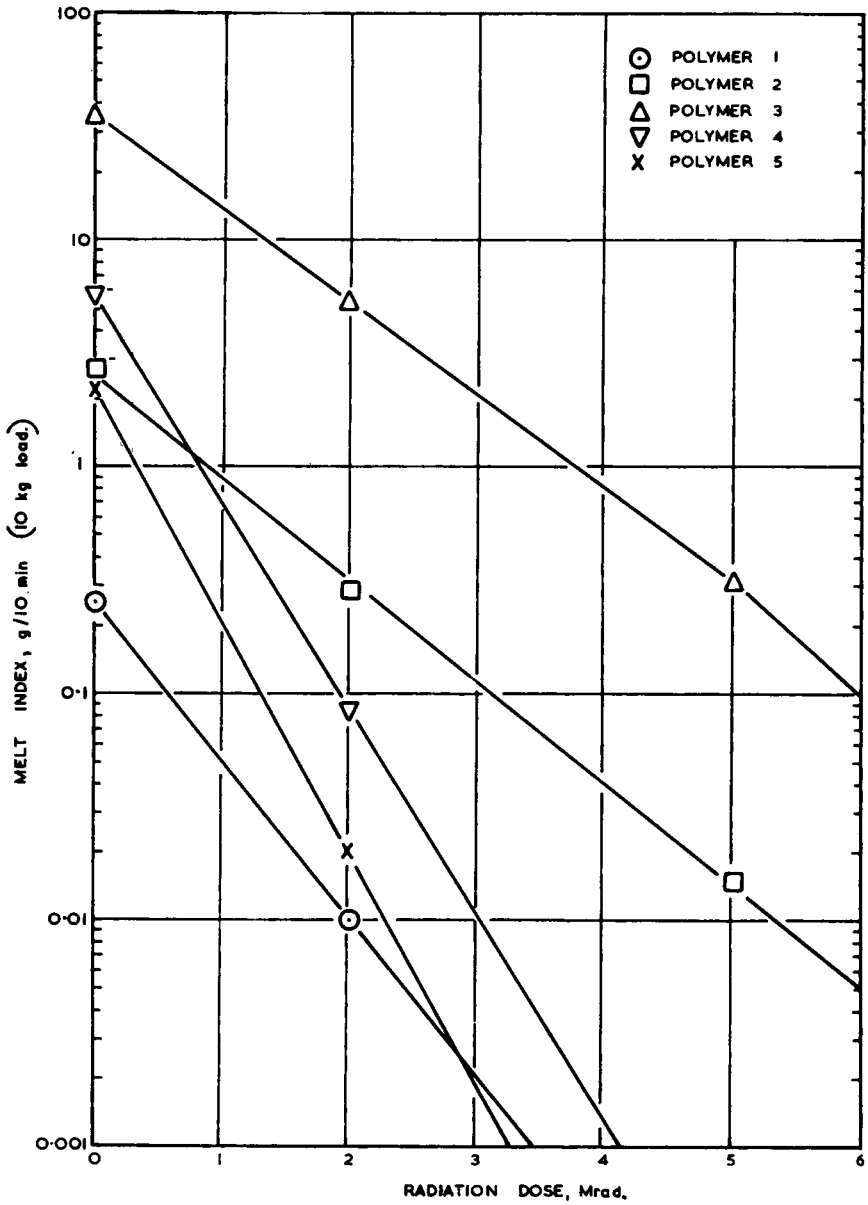

Fig. 1. Effect of electron radiation on melt index of polyethylenes.

TABLE II
Radiation Sensitivity of Melt Index of Ziegler Polyethylenes

Polymer	Melt index (10 kg. load) g./10 min.	Density, g./cc.	Radiation sensitivity of melt index[a]
1	0.25	0.947	0.69
2	2.6	0.948	0.45
3	35.0	0.950	0.41
4	5.7	0.953	0.91
5	2.2	0.956	1.02

[a] d log (melt index)/d (radiation dose).

In view of the rather small number of samples of measurable melt index which were available to us, we cannot claim any great accuracy for the above estimates of radiation sensitivity. Nevertheless, we still feel that they provide a useful guide for predicting the order of magnitude of radiation dose which will be required in any given situation.

A more extensive investigation of the effect of radiation on melt index of low density polyethylene has been made by Harper.[13] His results,

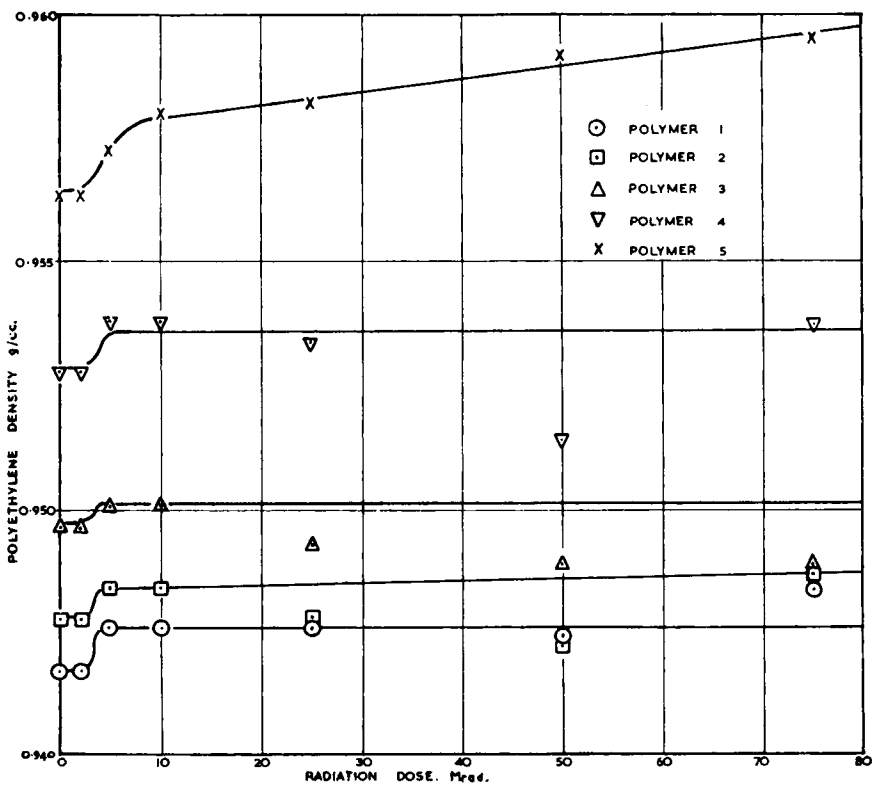

Fig. 2. Effect of electron radiation on density of polyethylenes.

when plotted as above, generally give lines which are rather less steep than ours; they are also distinctly curved. The reason for these differences is not clear, but it may be noted that Harper's polymers were much less crystalline and had higher melt indices than ours, and that he irradiated his samples in air whereas we used nitrogen.

Density

The most highly crystalline polymer examined shows a small but progressive increase in density with increasing radiation. A 75 Mrad dose increases its density from 0.956–0.959 (Fig. 2). The other four materials examined do not show progressive changes of this type. In all five materials, however, a small but distinct increment of density occurs between dose levels of 2 and 5 Mrad. This is attributed to thermal annealing of the test pieces caused by temperature rise during irradiation.

Softening Point

Electron radiation progressively elevates the softening point of all the polymers examined, but the effect is more marked in the case of polymers of low softening point (Fig. 3). The softening points of the three conventional Ziegler polymers increase on the average by 9°C. on radiation with 75 Mrad.

It should be noted that changes in softening point, determined according to the British Standard method used[7] do not reflect changes in crystalline

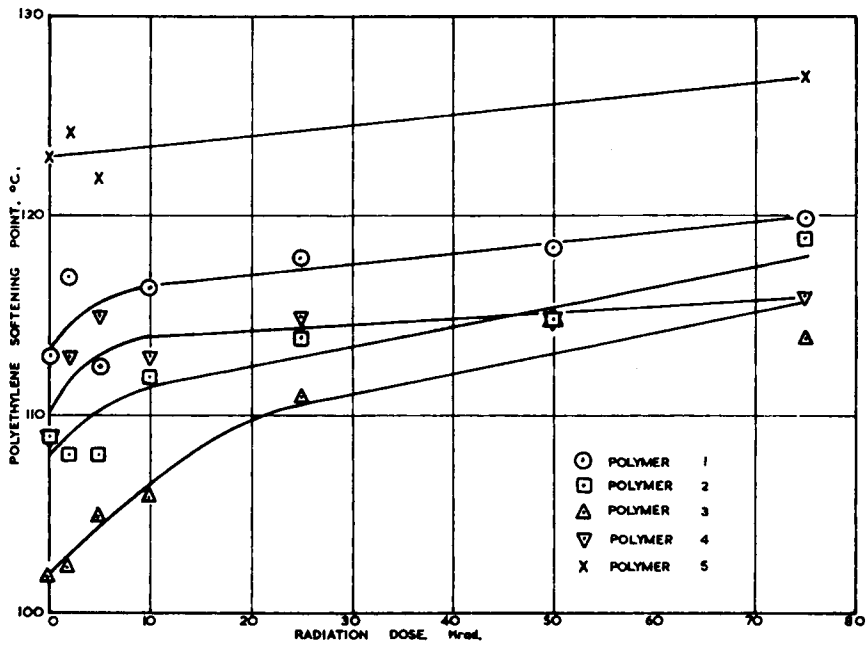

Fig. 3. Effect of electron radiation on softening point of polyethylenes.

melting point. Crystalline melting point in fact is lowered by electron radiation. It should also be noted that the observed elevations in softening point do not describe fully the increase in mechanical strength at high temperature which radiation confers on polyethylene. Crosslinked polyethylenes have such very poor flow, even at temperatures well above their softening points, that they possess the properties of flexible rubbers rather than of molten plastics.[14]

Tensile Properties

Yield stress increases slightly with increasing radiation dose (Fig. 4). At 75 Mrad, the most highly crystalline polymer shows the most marked increase (about 500 psi) whereas the other four polymers show a smaller increase (e.g., about 200 psi).

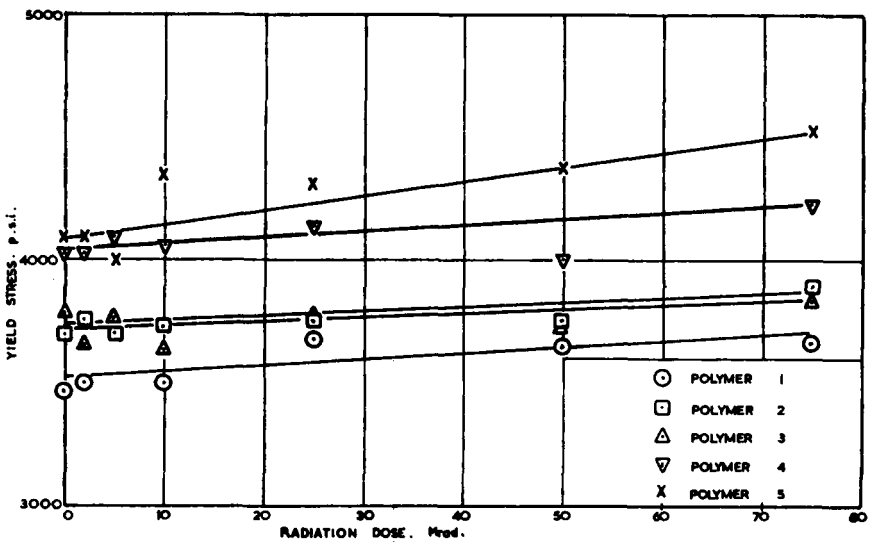

Fig. 4. Effect of electron radiation on tensile yield strength of polyethylene.

Ultimate tensile strength is affected in a complicated way by electron radiation (see Fig. 5). In two cases a small dose (5 Mrad) actually reduces the ultimate tensile strength and, in the other three cases, it causes no significant change. Large doses, however, (10 Mrad and more) generally increase the ultimate tensile strength, especially if it is low to start with. All five polymers have roughly the same ultimate tensile strength (about 4,400 psi) after the maximum dose (75 Mrad).

Ultimate elongation seems to be reduced to a common value of about 200% with a radiation dose of 50 Mrad (see Fig. 6). The effect of smaller doses is sometimes difficult to determine because there is some difficulty in reproducing ultimate elongation measurements when elongation is in the neighborhood of 300–600%.

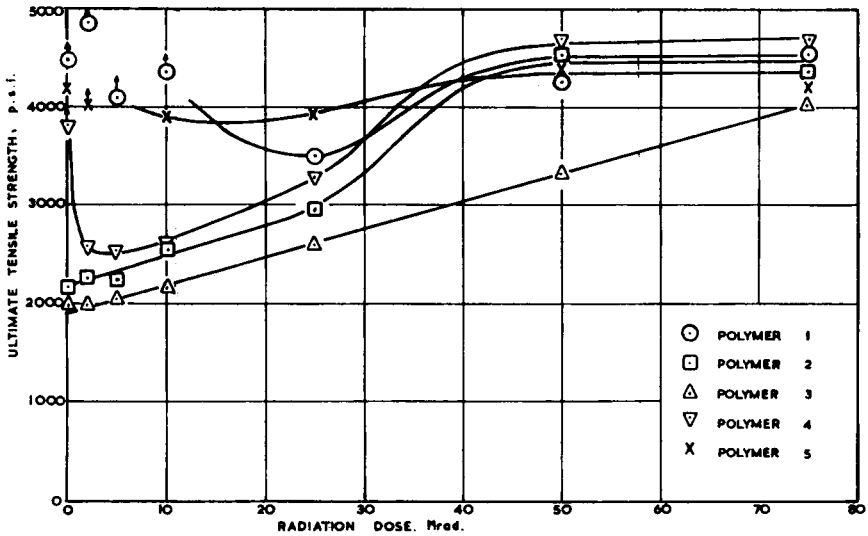

Fig. 5. Effect of electron radiation on ultimate tensile strength of polyethylenes.

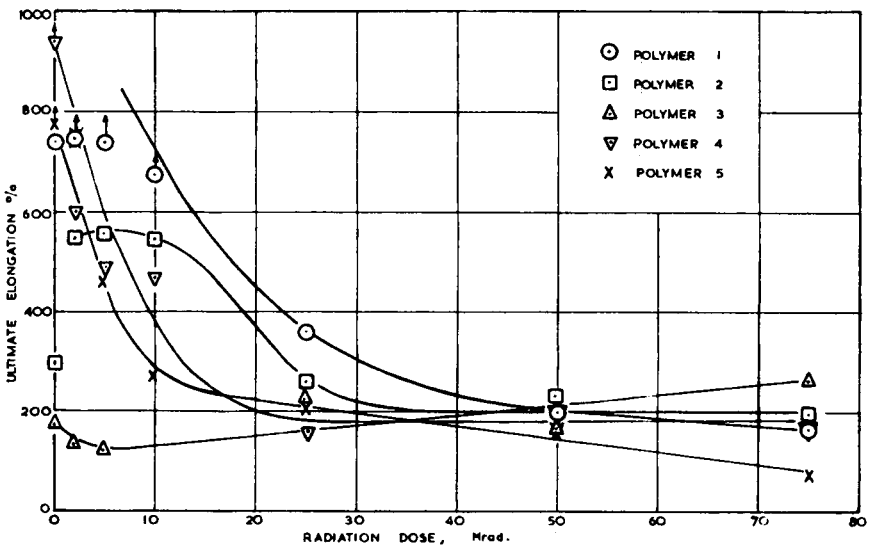

Fig. 6. Effect of electron radiation on ultimate elongation of polyethylene.

Impact Strength

Figure 7 shows that electron radiation up to a dose of 10 Mrad has practically no effect on the Izod impact strength of the four polymers examined. Larger doses cause a marked increase in impact strength in every case. At doses of 50 Mrad and, 75 Mrad, the impact strength rises to a common value of 15–20 ft. lb./in. notch.

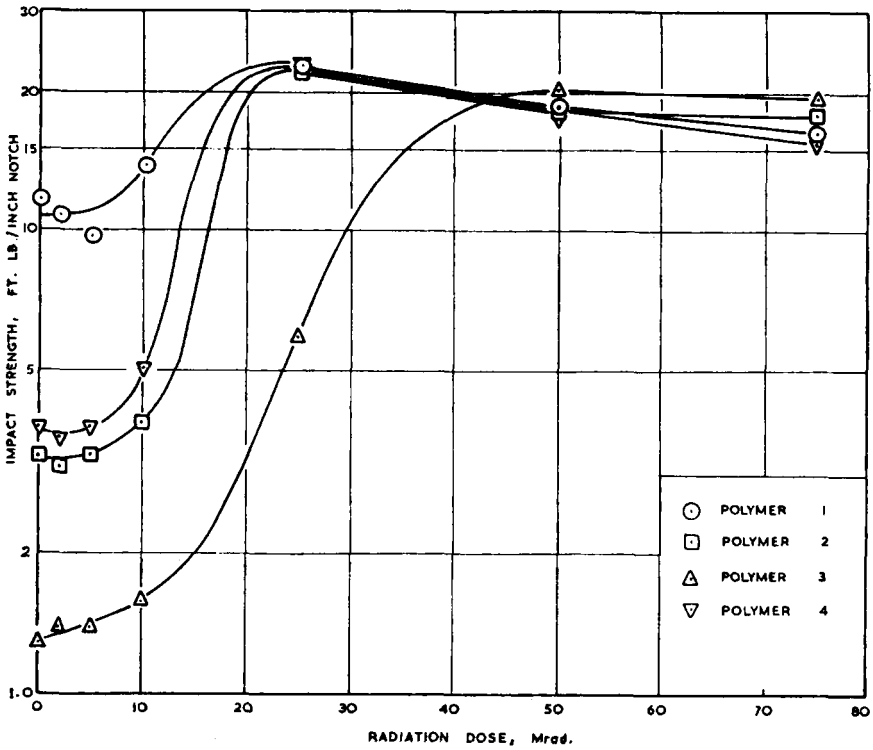

Fig. 7. Effect of electron radiation on impact strength of polyethylenes.

Power Factor

Figure 8 shows that in the case of all the polymers tested the effect of electron radiation first of all is to increase the power factor at 10^6 cycles/sec. At a dose of about 10 Mrad the power factor reaches a maximum and larger doses reduce the power factor again. These results are quite different from those of many published investigations. A possible explanation of these observations is that a small radiation dose decomposes the antioxidants which are present to give more polar products. This effect would increase the power factor of the polymer. Larger doses cannot increase the power factor any further, as no more antioxidant is available. A reduction of power factor can then occur by further decomposition of the polar products. In support of this suggestion it is interesting to note that the maximum power factor is obtained at the dose corresponding to that at which the last trace of pink color (due to the presence of di-β-naphthyl-p-phenylenediamine) disappears.

Lawton, Balwit, and Powell[15] have shown that irradiated high density polyethylenes contain trapped radicals which can survive for more than a thousand hours, even when the materials are stored in oxygen. Such polymers slowly accumulate an increasing concentration of carbonyl groups

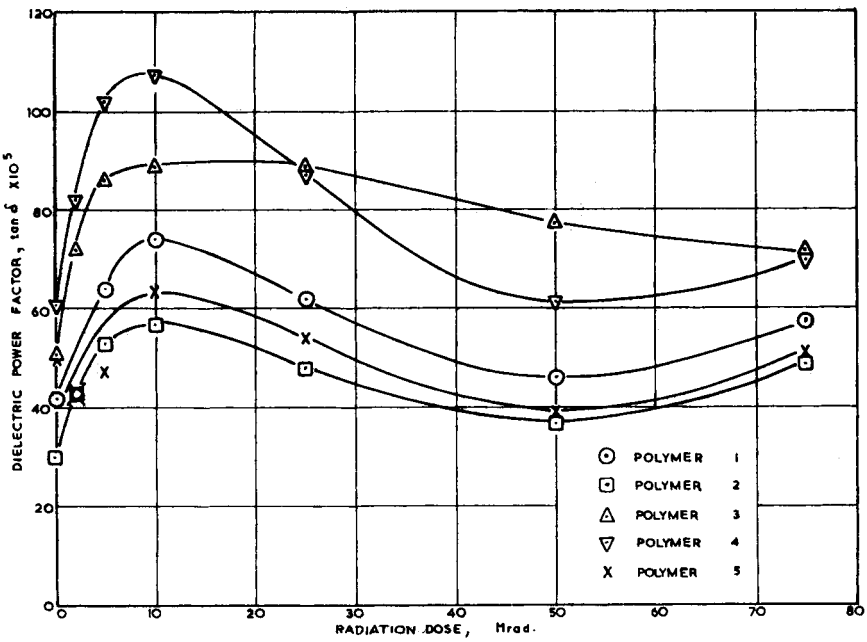

Fig. 8. Effect of electron radiation on power factor of polyethylenes.

during storage due to oxidation. It was of interest, therefore, to re-examine some of the irradiated polyethylenes at a later date to find out whether any increase in power factor had occurred. The results obtained two months later (Table I, figures in parentheses) do not show any consistent effect of storage in air on power factor and in all cases the observed changes are small.

Flex Resistance

The effect of electron radiation on flex resistance was examined in the case of Sample 2. Flex resistance here is the number of flexural deformations, in a Köhler-Molin folding endurance tester, which are required to break a standard test strip. Radiation reduces the flex resistance of the polymer rapidly at first and steadily thereafter. A 2 Mrad dose reduces the flex resistance to about 30% of its original value and a 50 Mrad dose reduces it to about 1%. The changes in flex resistance show remarkably little correlation with the changes in tensile properties and impact strength.

Environmental Stress-Cracking Resistance

The environmental stress cracking resistance of polyethylene is increased dramatically by electron radiation. This is true in the case of all five of the polymers examined, irrespective of their original behavior. A radiation dose of 10 Mrad improves the environmental stress-cracking resistance of the polymer in every case to a figure greater than 2,000 hr. The most

highly crystalline polyethylene (sample 5) achieves this level of performance at a radiation dose of only 5 Mrad.

The observed increase in environmental stress-cracking resistance caused by electron radiation seems to be of about the same order as would be expected from the decrease in melt index which also occurs. Consequently, irradiation of the polymer before fabrication into the finished article is unattractive; one might equally well employ a polymer of low melt index which has not been irradiated.

Irradiation of the polymer after fabrication, however, makes it possible to eliminate the danger of environmental stress-cracking altogether. For applications where this factor is of particular importance the use of electron radiation may, therefore, be commercially feasible. Indeed, commercial developments in the wire coating field have already been reported.[16,17] On the other hand the use of electron radiation represents an additional process for the fabricator, so that the further improvement in the quality of the polymers concerned, more particularly in respect of heat and environmental stress-cracking resistance, would represent a preferred solution for most applications.

CONCLUSIONS

The main effects of electron radiation on the properties of polyethylene are to decrease its melt index and to increase its resistance to environmental stress cracking. Density and softening point are changed only slightly. Ultimate tensile strength and impact strength increase with electron radiation, but very large doses (of the order of 25 Mrad) are required to effect a worthwhile improvement in these properties. Elongation and flex resistance are reduced.

The most promising applications for electron radiation are in the manufacture of articles of extremely high heat resistance or resistance to environmental stress cracking. In such cases the radiation would generally be applied to the articles after they had been shaped.

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Synopsis

An investigation has been made of the effects of electron radiation on the properties of stabilized Ziegler polyethylenes. Radiation was applied at dose levels of 0, 2, 5, 10, 25, 50, and 75 Mrad to polymers of various molecular weights and densities. The properties most affected were flow behavior and stress-cracking resistance. Radiation reduces the melt index of the polymers rapidly and no flow is observed at doses of 10 Mrad or more. A corresponding increase in environmental stress-cracking resistance is evident and in every case this property reaches a value of 2000 hr. at a dose of 10 Mrad. Changes in other properties are not very great until the radiation dose becomes large. At a dose of 50 Mrad, softening point is increased on the average by 7°C., yield strength is increased on the average by 140 psi, elongation is reduced to a common value of about 200% and impact strength is increased to a common value of about 20 ft. lb./in. notch. Power factor rises to a maximum as the dose is increased to 10 Mrad and diminishes at larger doses. Flex resistance, in the one case examined, diminishes as radiation dose is increased.

Résumé

On a fait une étude des effets des radiations électroniques sur les propriétés de: polyéthylènes stabilisés de Ziegler. On a appliqué une radiation de doses suivantess 0, 2, 5, 10, 25, 50, et 75 Mrad à des polymères de poids moléculaires et densités différents. Les propriétés les plus affectées sont le comportement à l'écoulment et la résistance à la tension de rupture. La radiation diminue rapidement l'induce de fusion des polymères et aucun écoulement n'a été observé à des doses de 10 Mrad ou plus. Une augmentation correspondante dans la résistance à la tension de rupture est évidente et dans chaque cas cette propriété atteint une valeur de 2,000 heures à une dose de 10 Mrad. Des changements dans d'autres propriétés ne sont pas très grands jusqu'au moment où la dose de radiation devient grande. A une dose de 50 Mrad, le point de ramollissement est augmenté de 7°C, en moyenne, la force de rendement est accrue en moyenne de 140 psi; l'élongation est reduite à une valeur courante d'environ 200% et la force d'impact est augmentée jusqu'à une valeur habituelle d'environ 20 ft. lb./in. notch. Le facteur de puissance s'élève jusqu'à une valeur maximum pour une dose augmentant jusque 10 Mrad et il diminue pour des doses plus fortes. Dans un cas étudié, la résistance à la flection diminue en fonction de l'augmentation de la dose.

Zusammenfassung

Eine Untersuchung des Einflusses von Elektronenbestrahlung auf die Eigenschaften von stabiliserten Ziegler-Polyäthylenen wurde durchgeführt. Es wurden Strahlungsdosen in der Höhe von 0, 2, 5, 10, 25, 50, und 75 Mrad bei Polymeren von verschiedenem Molekulargewicht und verschiedener Dichte angewendet. Die am stärksten beeinflussten Eigenschaften waren das Fliessverhalten und die Spannungsrissbeständigkeit. Die Bestrahlung setzt den Schmelzindex der Polymeren schnell herab und bei Dosen von 10

Mrad oder mehr kein Fliessen mehr beobachtet. Eine entsprechende Zunahme der Beständigkeit gegen milieubedingte Spannungsrissbildung ist augenscheinlich und diese Eigenschaft erreicht in allen Fällen einen Wert von 2000 h bei einer Dosis von 10 Mrad. Die Veränderungen anderer Eigenschaften sind nicht sehr bedeutend, bevor die Strahlungsdosis gross wird. Bei einer Dosis von 50 Mrad wird der Erweichungspunkt im Mittel um 7°C, die Fliessgrenze im Mittel um 140 psi erhöht, die Dehnung auf einen gemeinsamen Wert von etwa 200% herabgesetzt und die Schlagzähigkeit auf einen gemeinsamen Wert von etwa 20 ft. lb./in. Kerblänge erhöht. Der Verlustfaktor erreicht bei Erhöhung der Dosis auf 10 Mrad ein Maximum und nimmt bei grösseren Dosen Wieder ab. In dem einen untersuchten Fall nimmt die Biegefestigkeit mit steigender Bestrahlungsdosis ab.

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