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The Effect of Radiation on the Melt Index of Polyethylene

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There has been an increasing amount of work during the past several years on the effect of high energy radiation on the physical properties of polyethylene. Properties such as intrinsic viscosity,[1] solubility,[2] swelling, and elastic modulus[3] have been used to study the crosslinking of polyethylene induced by radiation.

The flow properties of molten polyethylene are also expected to change with radiation dose; if they would change in some uniform manner, a more convenient method for following the crosslinking induced by radiation might result. This paper reports the effect of radiation on the melt index of polyethylene.

EXPERIMENTAL

Irradiation

A General Electric Co. resonant transformer electron-beam generator was the source of radiation. The machine was operated at 1050 Kvp (peak) and 1.0 ma.[4]

The polyethylene was irradiated in the form of $^1/_8$-in. pellets. The pellets were irradiated in air by passing them through the electron beam. The depth of the pellets was so adjusted that the electron beam would just penetrate the entire layer. The samples were stirred after each pass through the beam. By passing the samples rapidly through the beam and stirring the samples after each pass the small temperature rise that accompanies radiation was minimized and each pellet received approximately the same uniform dose.

Materials

A variety of polyethylenes was studied: 410M (Dow Chemical Co.), 500E (Dow Chemical Co.), 700M (Dow Chemical Co.), Grex (Grace Chemical Co.), and Fortiflex (Celanese Chemical Co.).

Melt Index Determinations

The melt indices reported here were determined according to ASTM standard D1238-52T. All melt indices were determined in duplicate.

Dose Determinations

Cellophane dye dosimetry was used to determine the dose in these experiments. Du Pont 300 MSC light blue cellophane film was cut into strips $1^1/_2$ in. wide and 2 in. long. One of these pieces was taped over three of the four holes on a Beckman Model DU spectrophotometer sample holder. The holder was placed in the spectrophotometer and the initial transmittance at 6550 A. read. The sample holder was then situated on the conveyor belt with the film up and passed through the beam several times. The conditions for the cellophane irradiation were as near as possible the same as for the polyethylene pellet irradiation. The transmittance after irradiation was determined at 6550 A. with the Beckman Model DU spectrophotometer and the change in transmittance noted. The change was referred to a plot of change in transmission (ΔT) versus dose and the dose read and recorded. The plot of ΔT versus dose curve was prepared from the data of Henley and Richman[5] and by Atchison.[6]

RESULTS AND DISCUSSION

Three types of high pressure polyethylene and two types of low pressure polyethylene were irradiated at several doses each. The melt indices of these irradiated samples were determined and plotted versus dose. The graphs of these results are shown in Figures 1–5. Table I lists the experimental results. MI_0 designates the initial melt index.

An equation was found which accurately represents all of the curves shown. This equation was derived from a rate expression proposed by Klein[7]

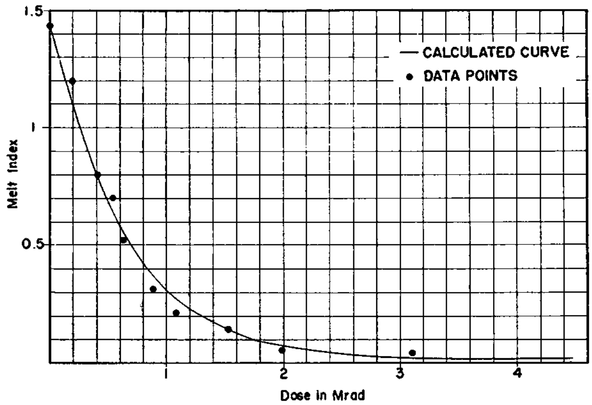

Fig. 1. Change in melt index of 410M polyethylene with radiation dose.

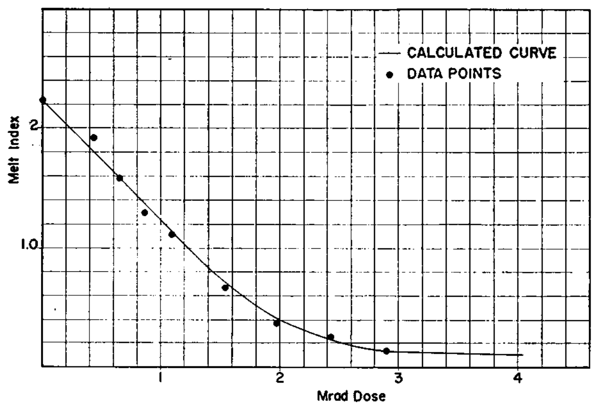

Fig. 2. Change in melt index of 500E polyethylene with radiation dose.

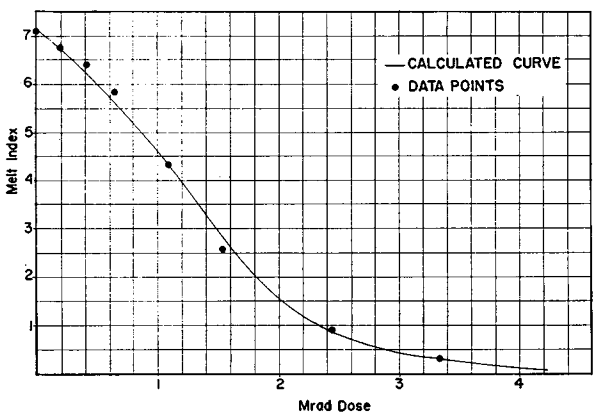

Fig. 3. Change in melt index of 700M polyethylene with radiation dose.

which will be published later. The Klein equation is:

$$dx/dt = k(x^* - x)/[1 + a(x^* - x) + b(x^* - x)^2]$$

where x is conversion of base reactant, x^* is the equilibrium conversion, and t is a time function.

The equation was altered as follows to represent these data. (*1*) Dose D (in megarads) was used instead at the time function t. (*2*) The change in melt index $(MI_0 - MI)/MI_0$ was taken as a measure of the conversion of base reactant x. (*3*) The $(MI_0 - MI)/MI_0$ value is taken as a measure of the conversion of base reaction and it approaches no equilibrium. The MI approaches zero with increasing dose and, therefore, the $(MI_0 - MI)/MI_0$

TABLE I
Experimental Results at 1 ma.

Polyethylene sample	Dose, Mrad	MI
410M (MI_0 = 1.45)	0.19	1.20
	0.42	0.80
	0.57	0.72
	0.64	0.52
	0.87	0.31
	1.09	0.21
	1.53	0.15
	1.99	0.05
	3.08	0.03
500E (MI_0 = 2.24)	0.19	2.08
	0.42	1.92
	0.64	1.58
	0.87	1.28
	1.09	1.13
	1.54	0.66
	1.99	0.38
	2.44	0.25
	2.88	0.12
700M (MI_0 = 7.09)	0.19	6.75
	0.42	6.40
	0.64	5.83
	1.09	4.34
	1.54	2.56
	2.44	0.89
	3.33	0.28
Grex (MI_0 = 4.20)	0.22	3.92
	0.44	3.29
	0.66	2.80
	0.88	2.39
	1.32	1.88
	1.76	1.21
	2.20	1.00
	3.08	0.35
Fortiflex (MI_0 = 5.22)	0.22	4.55
	0.44	3.77
	0.66	3.22
	0.88	2.92
	1.32	2.01
	1.76	1.43
	2.20	0.82
	3.08	0.43

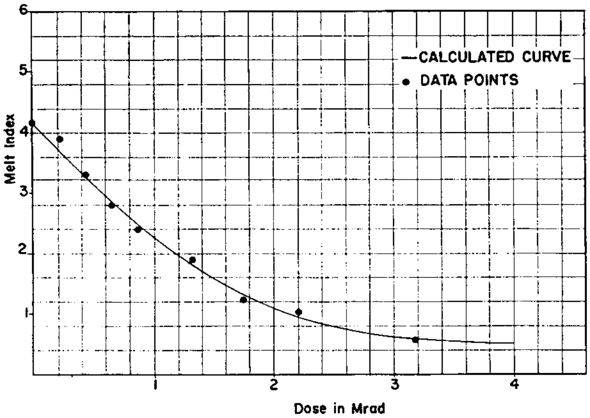

Fig. 4. Change in melt index of Grex polyethylene with radiation dose.

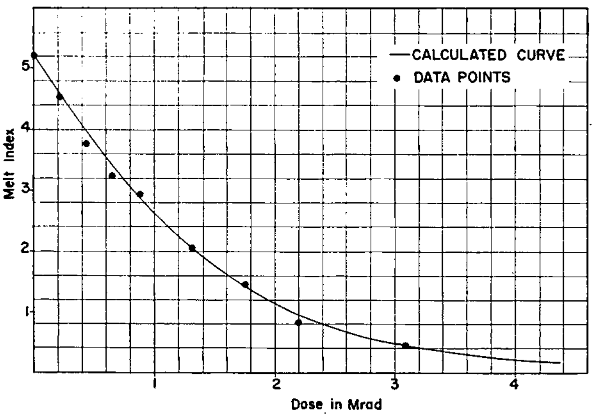

Fig. 5. Change in melt index of Fortiflex polyethylene with radiation dose.

value approaches unity. The equation then becomes

$$dx/dD = k(1 - x)/[1 + a(1 - x) + b(1 - x)^2]$$

where $x = (MI_0 - MI)/MI_0$ which, after integration, gives

$$D = \frac{a + b}{k} x - \frac{b}{2k} x^2 + \frac{2.303}{k} \log \frac{1}{1 - x}$$

This equation fits the MI vs. dose curve for all five types of polyethylene tested. The constants were determined with the use of an IBM 650 computer and are given in Table II.

TABLE II
Equation Constants

Sample	k	a	b
410M	0.944	−1.876	1.912
500E	1.219	−0.695	2.601
700M	0.962	−2.726	5.239
Grex	1.569	3.704	−2.074
Fortiflex	0.909	0.040	0.460

Effect of Radiation Dose Rate

The crosslinking of polyethylene is reported to be independent of radiation intensity.[8,9] Polyethylene 410M was irradiated at three different dose rates to see if this conclusion can be drawn from results obtained by use of the melt index as a measure of crosslinking.

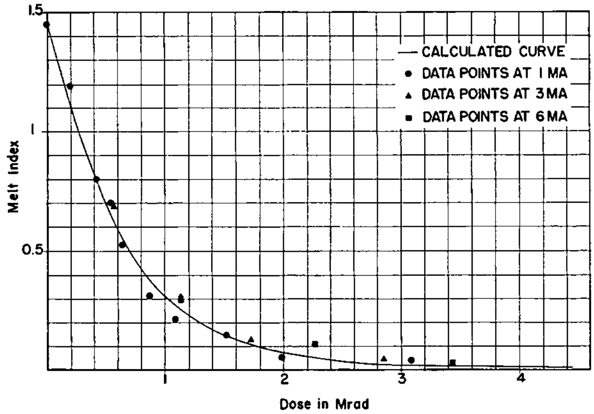

Fig. 6. Change in melt index of 410M polyethylene with radiation dose at three different dose rates.

The polyethylene pellets were irradiated in air as described earlier. The dose rates were varied by operating the electron beam generator at 1, 3, and 6 ma. At these amperages the dose rates are approximately 0.65, 1.95, and 3.90 Mrad/sec., respectively.

The data obtained with polyethylene 410M irradiated at 3 and 6 ma. fits the curve derived from the data obtained at 1 ma. very well and indicates that there is no dose rate effect. The data are reported in Table III and plotted in Figure 6.

TABLE III
Experimental Results at 3 and 6 ma.

Sample	Current, ma.	Dose, Mrad	MI
410M (MI_0 = 1.45)	3	0.57	0.68
	3	1.14	0.34
	3	1.72	0.14
	3	2.85	0.06
	6	1.14	0.30
	6	2.28	0.11
	6	3.42	0.03

CONCLUSIONS

These results show that the melt index of both high density and low density polyethylene changes uniformly with radiation dose. It indicates that melt index can be used as a measure of crosslinking. A relationship between melt index data and solubility data may exist such that the degree of crosslinking can be determined from melt index data. It is also likely that the effect of the initial properties of polyethylene on its susceptibility to radiation will be evident from the shape of the melt index vs. dose curves. Future work in this laboratory will be directed toward developing melt index as a means of following radiation-induced crosslinking.

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Synopsis

Five different types of polyethylene were irradiated in air and their melt indices determined as a function of the radiation dose. A resonant transformer electron beam generator was the source of radiation, and cellophane dye dosimetry was used to determine the radiation dose. The melt index was found to change uniformly with dose, and a single empirical equation was derived which describes the curves for all five types of polyethylene. By using the melt index as a measure of crosslinking, it was shown that the effect of radiation intensity on crosslinking is negligible.

Résumé

Cinq types différents de polyéthylène ont été irradiés à l'air et leurs indices de fusion ont été déterminés en fonction de la dose d'irradiation. Un transformateur à résonance, générateur de faisceux d'électrons, a été utilisé comme source de radiation et la dosimétrie à la cellophane colorée a servi à déterminer la dose de radiation. L'indice de fusion varie uniformément en fonction de la dose et une équation empirique permettant une description de diagramme pour les cinq types de polyéthylène a été établie. Les résultats faisant usage de l'indice de fusion comme mesure du pontage montrent que l'influence de l'intensité de la radiation sur le pontage est négligeable.

Zusammenfassung

Fünf verschiedene Polyäthylentypen wurden in Luft bestrahlt und ihr Schmelzindex als Funktion der Bestrahlungsdosis bestimmt. Ein Resonanzumwandler-Elektronenstrahlgenerator war die Strahlungsquelle und Cellophan-Farbstoffdosimetrie wurde zur Bestimmung der Strahlungsdosis benützt. Es wurde gefunden, dass sich der Schmelzindex in einheitlicher Weise mit der Dosis ändert und eine einzige empirische Gleichung wurde zur Darstellung der Kurven aller fünf Polyäthylentypen abgeleitet. Die Ergebnisse, die bei Verwendung des Schmelzindex als Mass für die Vernetzung erhalten wurden, zeigen dass der Einfluss der Strahlungsintensität auf die Vernetzung vernachlässigbar ist.

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