Effects of γ-Ray Irradiation on Polymers. (II)

Effect of γ-Ray Irradiation on Mechanical Psoperties of Filaments of Low Density Polyethylene

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The changes in mechanical properties of low density polyethylene filaments elongated to various degrees by γ-ray irradiation were studied. The tensile strength of the irradiated filaments changed slightly with dose up to 10^7 r, but at higher doses it increased by vacuum-irradiation and decreased by air-irradiation. Young's modulus and degree of elasticity of the irradiated samples at 65% RH and 20°C hardly changed. The changes of these mechanical properties with irradiation appear to be independent of the degree of elongation. The percent shrinkage of the samples decreased with dose, and their flow point was raised in vacuum-irradiation but lowered in air.

INTRODUCTION

In the preceding paper,[1] solubility and density had been studied of low and high density polyethylene filaments irradiated in vacuum and in air. With the same purpose as that of the preceding paper, mechanical and thermal properties of low density polyethylene filaments elongated to various degrees by γ-ray irradiation will be studied in this paper.

MATERIALS AND IRRADIATION

Materials and condition of irradiation were the same as those described in the preceding paper[1].

RESULTS AND DISCUSSION

(1) Tensile Strength and Elongation

The Instron Tensile Test Machine was used in performing the stress-strain measurements, which furnishes an automatic record of load *vs.* elongation curve during each test period. The test specimen was 5 cm length and was streched at a rate of 10 cm/min. The test was carried out at 65% RH and 20°C. The changes of tensile strength and elongation of the samples with dose are given in Tables 1 and 2.

Tensile strength of the vacuum-irradiated polyethylene generally increased with dose irrespective of the degree of elongation, whereas that of the air-irradiated filaments increased slightly with dose up to 10^7 r and in a higher dose range decreased again. The elongation of the samples increased with

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Table 1. Changes of tensile strength (kg/mm²) by irradiation.

Sample	Unirradiated	Vacuum-irradiation Dose×10⁻⁶ r					Air-irradiation Dose×10⁻⁶ r				
		2.4	8.2	15	35	99	2.4	8.2	15	35	99
L-1	1.68	1.81	2.05	2.27	2.68	2.99	1.65	1.88	1.81	1.20	0.77
L-3	3.92	3.49	5.18	5.16	5.51	4.42	3.29	4.36	4.26	2.16	1.59
L-4	5.58	5.44	4.78	5.36	6.49	5.52	4.99	3.79	4.79	2.90	1.48
L-5	7.81	9.40	9.73	8.25	13.67	9.56	9.60	8.58	7.69	5.14	—

Table 2. Changes of elongation (%) by irradiation.

Sample	Unirradiated	Vacuum-irradiation Dose×10⁻⁶ r					Air-irradiation Dose×10⁻⁶ r				
		2.4	8.2	15	35	99	2.4	8.2	15	35	99
L-1	739	812	743	730	610	338	683	732	690	536	11
L-3	222	226	270	226	186	96	218	240	232	138	11
L-4	120	186	123	129	112	53	123	117	120	65	5
L-5	60	58	69	98	57	37	74	64	60	37	—

irradiation up to 10^7 r and began to decrease at a still higher radiation dose, in both cases in which the irradiation was carried out. For high irradiation levels, the elongation of the air-irradiated samples decreased steeply. From this experiment, tensile properties were not found to change systematically with degree of elongation by irradiation. The changes in the tensile strength and elongation by the vacuum-irradiation appear to be caused by increasing restriction of the motion of molecular segments through crosslinking. A sharp drop in the tensile strength and elongation by the air-irradiation appears to depend on oxidation. These experimental results are similar to those reported by Lawton[2], Kawai *et al.*[3] recently.

(2) Load-elongation Curve

Load *vs.* elongation curves obtained at different irradiation levels up to 9.9×10^7 r are illustrated in Figs. 1 to 4. The shape of the load-elongation curve is influenced by dose. When the irradiation was carried out in vacuum, the shape of these curves up to the yield point is independent of the dose. The resistance for stretching rises considerably with dose after the yield point. Since crosslinking reactions occur mainly in the amorphous region,[4] it may be assumed that the shape of the curve at the initial stage which depends on the crystallinity did not change with dose, whereas at higher stretchings, the shape changed significantly above 1.4×10^7r due to crosslinking. This appears to be caused by main-chain scission and oxidation by the irradiation. The changes in load *vs.* elongation curve with dose is independent of the difference in the degrees of elongation of filaments.

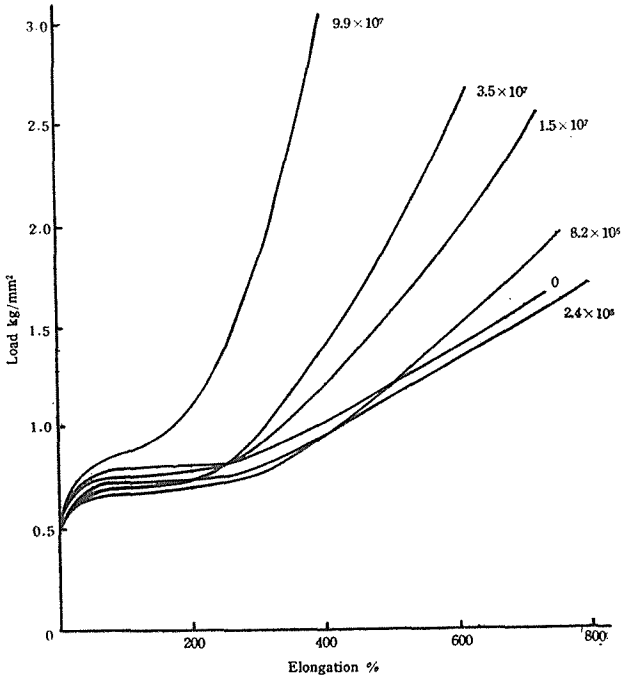

Fig. 1. Load-elongation curves of vacuum-irradiated unelongated filaments. (L-1)

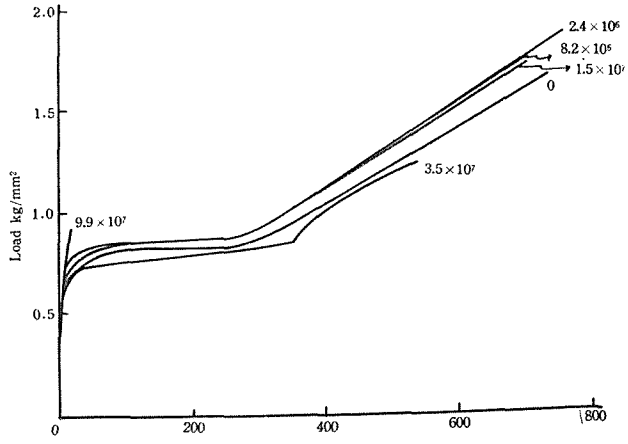

Fig. 2. Load-elongation curves of air-irradiated unelongated filaments. (L-1)

(3) Young's Modulus

Young's modulus was measured by the Instron Test Machine at RH 65% and 20°C. and at 1% elongation. The specimen was 5 cm length and stretched at a constant rate of 0.5 cm/min. during each test. The results are listed in Table 3.

In our experiments, Young's modulus did not change markedly in air- and vacuum-irradiation except at higher doses[5,6,7]. As described above, at higher stretchings there was an increase in the resistance for stretching.

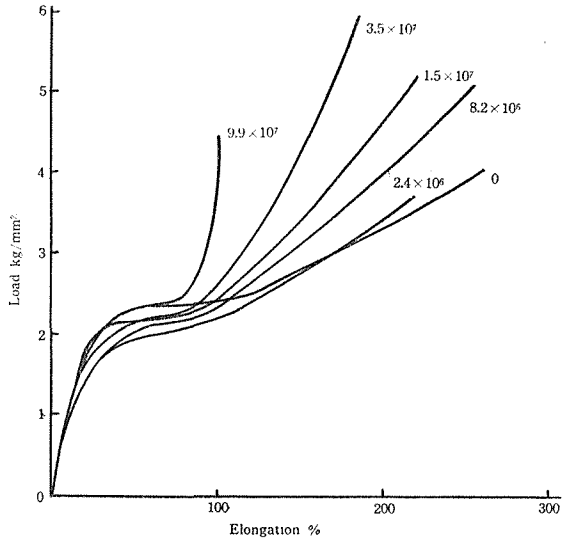

Fig. 3. Lood-elongation curves of the vacuum-irradiated filaments elongated to three times. (L-3)

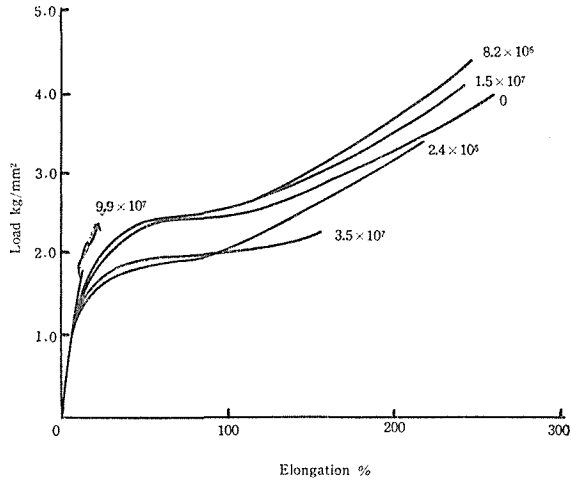

Fig. 4. Load-elongation curves of the air-irradiatod filaments. (L-3)

Table 3. Changes of Young's modulus (kg/mm²) by irradiation.

Sample	Unirradiated	Vacuum-irradiation Dose×10⁻⁶ r					Air-irradiation Dose×10⁻⁶ r				
		2.4	8.2	15	35	99	2.4	8.2	15	35	99
L-1	99	93	101	107	87	109	122	106	115	114	150
L-3	143	106	128	120	122	139	115	152	153	141	225
L-4	220	209	189	189	221	244	243	189	266	277	305
L-5	418	466	466	466	538	470	509	466	422	446	—

Measurements of Young's modulus at higher temperatures may furnish different results from ours.

(4) Degree of Elasticity

The degree of elasticity was measured using the Instron Tensile Test Machine and at 65% RH and 20°C. The length of specimen was 5 cm and stretched at a constant rate of 2 cm/min. up to a given percentage of elongation. The degree of elasticity was estimated from a decrease of the length after the given load was removed. The degree of elasticity as a function of elongation at any dose are shown in Figs. 5 and 6.

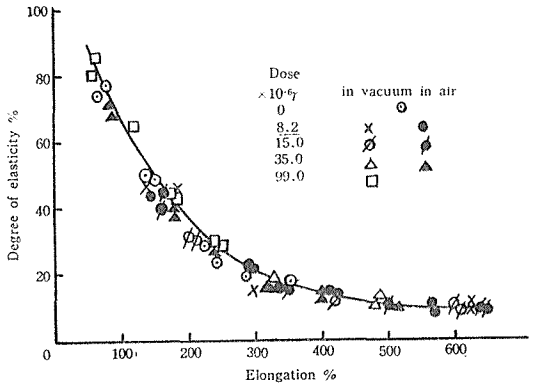

Fig. 5. Degree of elasticity of irradiated unelongated filaments at any dose as a function of elongation.

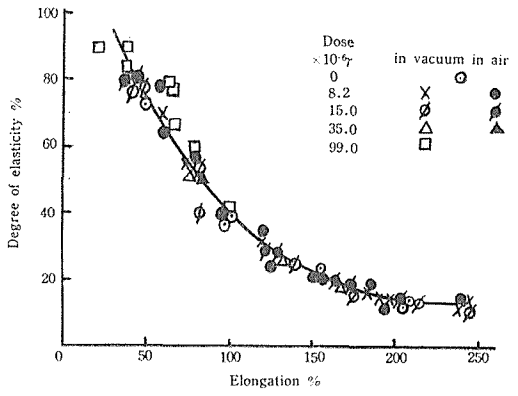

Fig. 6. Degree of elasticity of irradiated filaments elongated to three times (L-3) as a function of elongation.

The degree of elasticity does not show a change with dose, in spite of the variation of the chemical structure of the polymers.

(5) Shrinkage by Heating

Percent shrinkage by heating without load was measured with the use of

a cathetometer. The specimens were heated up at a constant rate of 1°C/min. The temperature dependence of shrinking at any dose is displayed in Figs. 7 to 10. The percent shrinkage of the unirradiated samples is larger than that of irradiated samples at any temperature, and the samples irradiated to higer doses shrink only slightly.

The flow point of vacuum-irradiated samples rises with dose and the

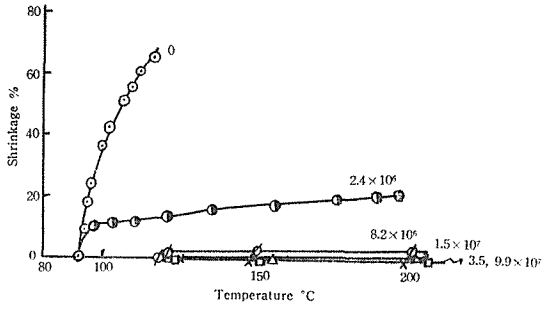

Fig. 7. Percent shrinkage–Temperature curves of the vacuum-irradiated unelongated filaments at any dose.

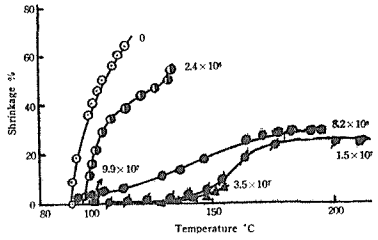

Fig. 8. Percent shrinkage–Temperature curves of the air-irradiated unelongated filaments at any dose.

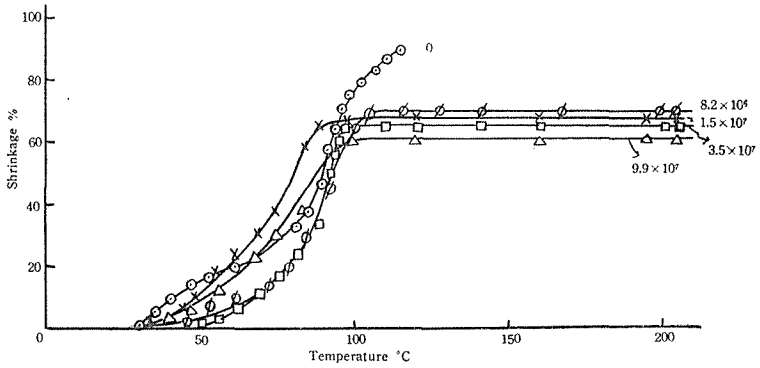

Fig. 9. Percent shrinkage–temperaturc curves of the vacuum-irradiated filaments. (L-4)

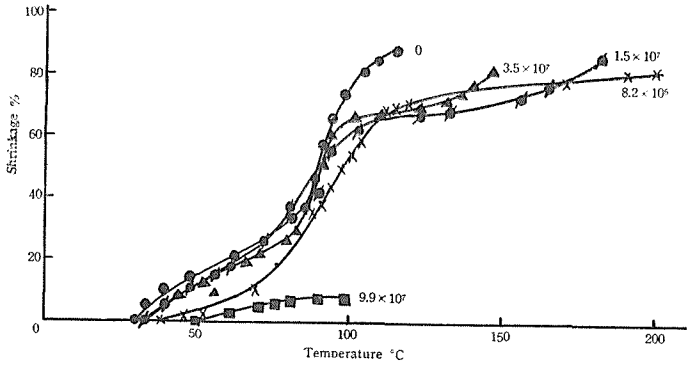

Fig. 10. Percent shrinkage–temperature curves of the air-irradiated filaments. (L-4).

samples become yellow at about 205°C. As for the unelongated filaments irradiated in air, the flow point rised with dose below 10^7 r and in a higher dose range sinked. The irradiated samples elongated to four-times began to shrink about at the same temperature as for the unirradiated ones. The percent shrinkage for elongated samples irradiated in air increased to 70% with elevating temperature, and above 120°C slightly. At lower doses, the flow point of air-irradiated samples elongated increased with dose and above 3.5×10^7 r decreased again. The flow point for the unelongated samples appears generally to be higher than that for the elongated ones at the same dose.

Table 4. Flow point (°C) of air-irradiated samples.

Sample	Unirradiated	Dose $\times 10^{-6}$ r				
		2.4	8.2	15	35	99
L-1	115	133	193	209	153	102
L-4	115	—	195	182	145	99

The experimental results of air-irradiated samples at any dose are given in Table 4.

The shrinking may depend on the degrees of crystallinity and of crosslinking. Then, the percent shrinkage of the vacuum-irradiated samples would decrease with dose at higher doses, since a large number of crosslinking was produced, enough to stiffen the chain. On the other hand, the shrinkage of the air-irradiated samples appears to be due to crosslinking and main-chain scission. It is hard to see whether the degree of elongation has an effect on the flow point of the air-irradiated filaments or not.

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