

# Effects of $\gamma$ -Ray Irradiation on Polymers. (III)

## Effects of $\gamma$ -Ray on Mechanical Properties of Filaments of High Density Polyethylene

Ichiro SAKURADA, Waichiro TSUJI and Fujiko KIMURA\*

Sakurada Laboratory, Institute for Chemical Research, Kyoto University

(Received August 10, 1959)

For comparison with the low density polyethylene, the effects of irradiation on the mechanical properties were studied of the high density polyethylene filaments. By the vacuum-irradiation, the tensile strength decreased with dose for the unelongated and lowly elongated samples, whereas it was practically constant for the highly elongated samples. On the other hand, the tensile strength of the air-irradiated samples decreased considerably with dose. Young's modulus and degree of elasticity at 65% RH and 20°C were insensitive to dose, just as those of the low density polyethylene. The percent shrinkage of the irradiated filaments decreased with dose, and the flow point rose in vacuum irradiation but fell in air-irradiation.

### INTRODUCTION

In the preceding papers<sup>1,2)</sup>, the changes by the air- and vacuum-irradiations of the solubility and density of low and high density polyethylene filaments were compared, and the change of mechanical properties of low density polyethylene filaments through irradiation were studied. Using the high density polyethylene filaments elongated to various degrees, the changes of the mechanical and thermal properties by  $\gamma$ -ray irradiation will be reported in this paper.

### MATERIALS AND IRRADIATION

The materials and the condition for irradiation were described in the preceding papers<sup>1)</sup>.

### RESULTS AND DISCUSSION

The measurements of the mechanical and thermal properties were carried out in the same manner as that described in the preceding papers<sup>2)</sup>.

#### (1) Tensile Strength and Elongation

The changes in tensile strength and elongation with dose are tabulated in Tables 1 and 2.

The tensile strength drops with dose both in air and in vacuum except the case of the highly elongated sample. The tensile strength of the air-

---

\* 桜田 一郎, 辻 和一郎, 木村 藤子

γ-Ray Irradiation on Polymers. (III)

Table 1. Changes of tensile strength (kg/mm<sup>2</sup>) by irradiation.

Sample	Unirradiated	Vacuum-irradiation Dose × 10 <sup>-6</sup> r					Air-irradiation Dose × 10 <sup>-6</sup> r				
		2.4	8.2	15	35	99	2.4	8.2	15	35	99
H-1	5.79	5.75	4.63	4.52	3.67	4.37	5.01	3.03	1.79	—	—
H-3	18.74	16.88	16.04	13.87	9.83	11.56	11.79	8.35	5.89	—	—
H-5	33.09	23.44	21.58	20.75	22.07	21.16	17.39	13.37	11.22	—	—
H-6	35.93	31.89	32.79	31.04	31.29	29.66	28.12	17.79	15.38	—	—

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

Sample	Unirradiated	Vacuum-irradiation Dose × 10 <sup>-6</sup> r					Air-irradiation Dose × 10 <sup>-6</sup> r				
		2.4	8.2	15	35	99	2.4	8.2	15	35	99
H-1	939	1058	802	886	494	305	1192	1068	942	—	—
H-3	198	224	209	197	123	76	289	294	251	—	—
H-5	55	41	50	46	46	28	52	55	12	—	—
H-6	37	47	45	47	46	28	34	26	14	—	—

irradiated filaments decreases more steeply than that of the vacuum-irradiated one. It is interesting to note a different tendency in the strength of highly elongated filaments irradiated in vacuum: the strength is independent of the irradiation. The properties of filaments irradiated above  $3.5 \times 10^7$  r in air could not be measured, because the samples became too brittle by irradiation.

The elongation of the irradiated filaments increased up to  $10^7$  r and at higher doses began to decrease again with dose. It is difficult to analyse this result because of the possible presence of the catalyst in the high density polyethylene. The decrease in the tensile strength of the high density polyethylene appears to depend on the main-chain scission. As for this result Slichter<sup>3)</sup> and Lawton *et al.*'s<sup>4)</sup> idea is suggestive that high energy irradiation causes degradation concurrently in the crystalline and amorphous regions and the crosslinking reaction occurs mainly in the amorphous region. The considerable decrease of the strength of air-irradiated filaments seems to be due to oxidation.

### (2) Load vs. Elongation Curve

The load vs. elongation curves at various doses are shown in Figs. 1 to 8.

As for the unelongated filaments and the three-times elongated ones irradiated in vacuum, the shape of the curve hardly varies with dose up to  $10^7$  r, but remarkably at a still higher dose: the resistance for stretching at higher stretching increases by irradiation. The shape of the curve of highly elongated filaments irradiated in vacuum appears to be independent of the irradiation. The load vs. elongation curve of the air-irradiated filaments depends on dose

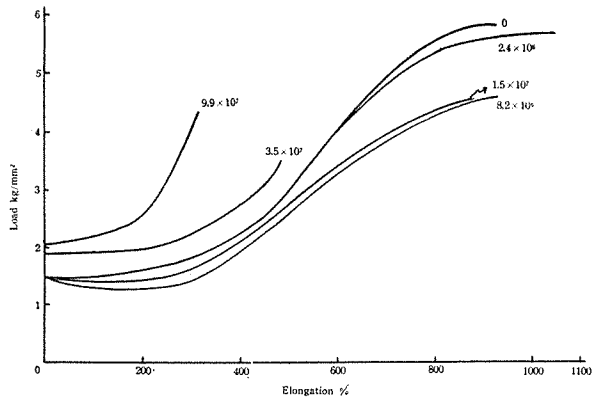


Fig. 1. Load-elongation curves of the vacuum-irradiated unelongated filaments. (H-1)

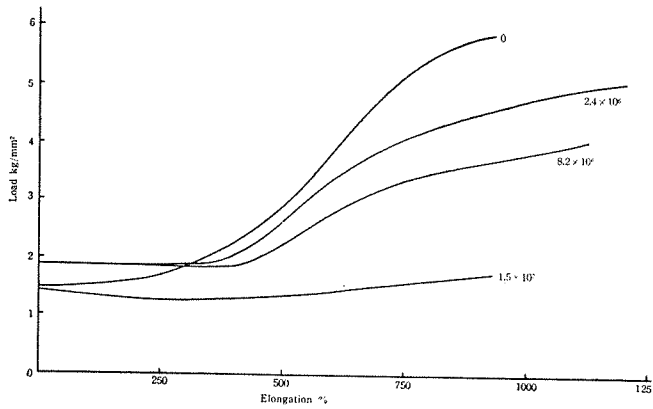


Fig. 2. Load-elongation curves of the air-irradiated unelongated filaments. (H-1)

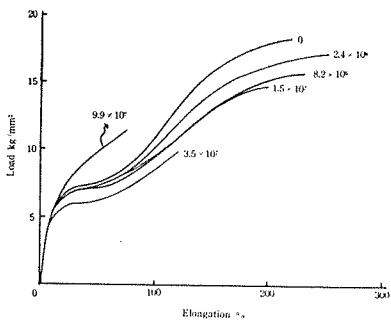


Fig. 3. Load-elongation curves of the vacuum-irradiated filaments. (H-3)

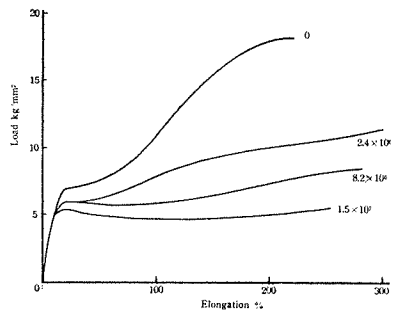


Fig. 4. Load-elongation curves of the air-irradiated filaments. (H-3)

γ-Ray Irradiation on Polymers. (III)

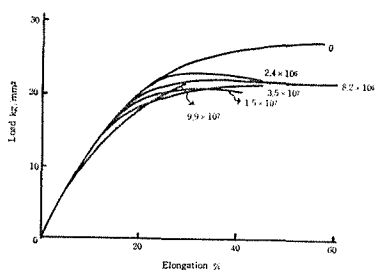


Fig. 5. Load-elongation curves of the vacuum-irradiated filaments. (H-5)

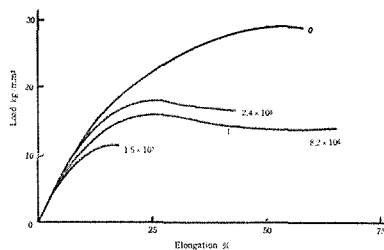


Fig. 6. Load-elongation curves of the air-irradiated filaments. (H-5)

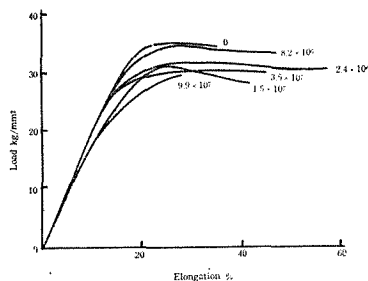


Fig. 7. Load-elongation curves of the vacuum-irradiated filaments. (H-6)

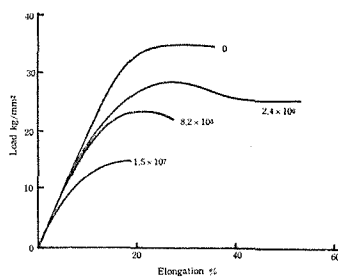


Fig. 8. Load-elongation curves of the air-irradiated filaments. (H-6)

also.

(3) Young's Modulus

Young's modulus is given in Table 3.

Table 3. Changes of Young's modulus (kg/mm<sup>2</sup>) by irradiation.

Sample	Unirradiated	Vacuum-irradiation Dose × 10 <sup>-6</sup> r					Air-irradiation Dose × 10 <sup>-6</sup> r				
		2.4	8.2	15	35	99	2.4	8.2	15	35	99
H-1	461	425	462	457	419	621	494	462	387	—	—
H-3	886	790	946	771	675	983	809	979	1002	—	—
H-5	1616	1411	1439	1439	1587	1499	1322	1591	1557	—	—
H-6	2059	1602	2118	2029	2207	1922	2279	2161	1994	—	—

Though the resistance for stretching at higher stretchings decreases with dose, Young's modulus is nearly independent of dose. This appears to be reasonable. But it may change with dose at higher temperatures.

(4) Degree of Elasticity

The degree of elasticity is plotted against elongation in Figs. 9 and 10. It does not change remarkably with dose in the case of the unelongated samples irradiated in vacuum but declines slightly for the air-irradiated samples. The degree of elasticity of the elongated samples also does not change with dose,

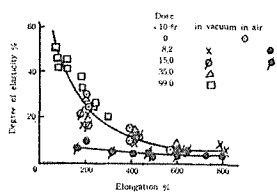


Fig. 9. Degree of elasticity as a function of elongation at any dose of unelongated filaments.

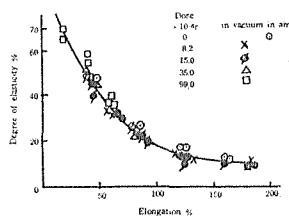


Fig. 10. Degree of elasticity at any dose as a function of elongation of elongated filaments.

whether the irradiation was carried out in vacuum or in air. Insensitivity of the degree of elasticity towards dose is interesting, compared with dose dependences of solubility and tensile properties.

### (5) Shrinkage by Heating

The percent shrinkage as a function of temperature is shown in Figs. 11 to 14. In the case of unelongated sample irradiated in vacuum the percent shrinkage at the same temperature decreased regularly with dose. The flow point of the vacuum-irradiated filament was elevated with dose. All irradiated samples began to shrink at 115°C and shrank gradually up to 170°C. At higher temperatures the samples shrank little with temperature. The samples irradiated in vacuum above  $1.4 \times 10^7$  r became yellow at 200°C. The percent shrinkage of the samples irradiated in air from  $2.4 \times 10^6$  r to  $1.5 \times 10^7$  r decreased with dose and the samples irradiated at  $9.9 \times 10^7$  r in air flowed at about 100°C

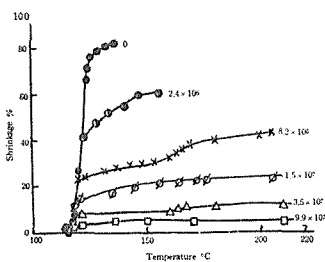


Fig. 11. Percent shrinkage-temperature curves of vacuum-irradiated unelongated filaments.

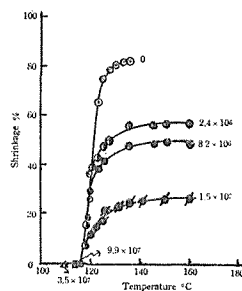


Fig. 12. Percent shrinkage-temperature curves of air-irradiated unelongated filaments.

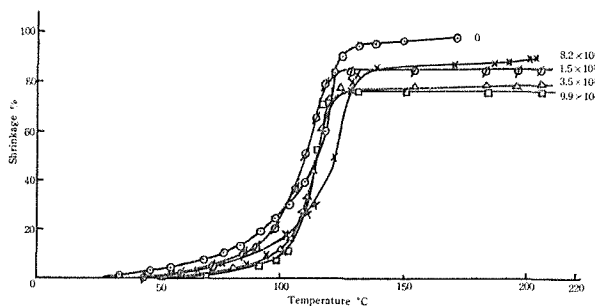


Fig. 13. Percent shrinkage-temperature curves of the vacuum-irradiated filaments. (H-5)

γ-Ray Irradiation on Polymers (III)

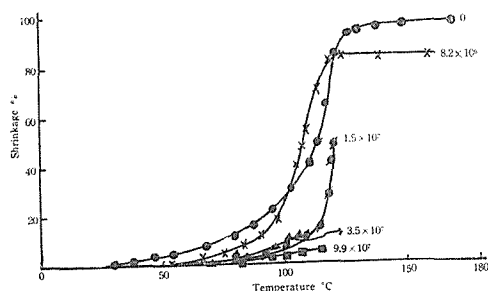


Fig. 14. Percent shrinkage-temperature curves of the air-irradiated filaments. (H-5)

without shrinking. At the same dose, the percent shrinkage of the vacuum-irradiated samples at the same temperature was larger than that of the air-irradiated ones. The percent shrinkage of the high density polyethylene appears to be smaller than that of the low density polyethylene. The irradiated samples elongated to five-times shrank slowly with temperature from room temperature to 120°C but only a little at higher temperatures. As in the unelongated samples, the flow point of the elongated samples irradiated in air was lowered with dose.

The flow point of these air-irradiated samples is given in Table 4.

Table 4. Flow point of air-irradiated samples.

Sample	Unirradiated	Dose $\times 10^{-6}$ r		
		15	35	99
H-1	135	162	116	110
H-5	135	121	106	115

As described on the low density polyethylene, the shrinking appears to depend on the degrees of crosslinking and of crystallinity.

The decrease in the percent shrinkage of these samples would be ascribed mainly to the crosslinking for the vacuum-irradiated filaments, and to the degradation for the air-irradiated ones. The changes of the flow points of the irradiated samples would also be due to crosslinking and degradation.

REFERENCES

- (1) I. Sakurada, W. Tsuji and F. Kimura, *This Bulletin*, **37**, 353 (1959).
- (2) I. Sakurada, W. Tsuji and F. Kimura, *This Bulletin*, **37**, 361 (1959).
- (3) W. P. Slichter and E. R. Mendell., *J. Phys. Chem.*, **62**, 334 (1958).
- (4) E. J. Lawton, J. S. Balwit and R. S. Powell, *J. Polymer Sci.*, **32**, 257, 277 (1958).