Effects of γ-Ray Irradiation on Filament of Isotactic Polypropylene

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Studies have been carried out on the effects of γ-ray irradiation on physical and mechanical properties of isotactic polypropylene filament. Samples were irradiated in the presence of air as well as in vacuo at room temperature. The densities of the samples were almost unchanged by irradiation *in vacuo*, but considerably increased in case of irradiation in air.

The degree of shrinkage at the flow temperature of the irradiated filament as well as the flow temperature decreased with increase in dose, except for a sample irradiated at a dose of 9.3×10^7r *in vacuo*. The tensile strength and elongation at break decreased by irradiation in vacuo, especially in air.

Young's modulus and elastic recovery at room temperature did not change with dose. The changes in these properties by irradiation are presumed to be dependent on the presence of oxygen.

1. INTRODUCTION

Previously the changes of physical and mechanical properties had been reported of low and high density polyethylene filaments irradiated by γ-ray *in vacuo* as well as in air[1)~3)]. In view of the molecular structure, it is desirable to investigate the radiation induced changes of polypropylene which has an intermediate structure between polyethylene and polyisobutylene. Black and Lyons[4),5)], by the use of electron beams, found that crosslinking only slightly exceeds degradation for polypropylene, and thus both the radiation dose at gel point and the limiting sol fraction are high. Yamada and Aoki,[6)] and Sofue, Tabata and Tajima[7),8)] had reported the same results on the effects of γ-ray irradiation on solubility and molecular weight.

In this paper, the radiation induced changes in density, thermal and mechanical properties will be discussed on monofilament of isotactic polypropylene, both unoriented and oriented by stretching, since it is interesting to study the effect of irradiation on the degree of crystallinity and of orientation of the sample.

2. EXPERIMENTAL

2.1) Materials

Filaments of isotactic polypropylene were made from Moplen AS.

The samples used in this investigation were the filaments of 100 and 20 deniers, the latter was prepared by the elongation of the former at 100°C. According to

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the results reported by Sakurada and Nukushina[9], the crystallinity of these filaments was 39 and 52% respectively.

2.2) Irradiation

Irradiation was carried out in glass tubes sealed under vacuum of 10^{-4}mm Hg or in air, at room temperature, making use of a 200 curie cobalt 60 source of the Institute for Chemical Research, Kyoto University. The sample was irradiated up to a dose of 9.3×10^{7}r *in vacuo* and of 3.1×10^{7}r in air with a dose rate of 7×10^{4}r/hr.

3. EXPERIMENTAL RESULTS

3.1) Density

The densities of these filaments irradiated *in vacuo* and in air were measured by a floatation method in water-ethylalcohol mixture at 25°C[10]. The change in the density as a function of radiation dose is shown in Fig. 1. The density of the filament increased with radiation dose scarcely *in vacuo* but remarkably in air.

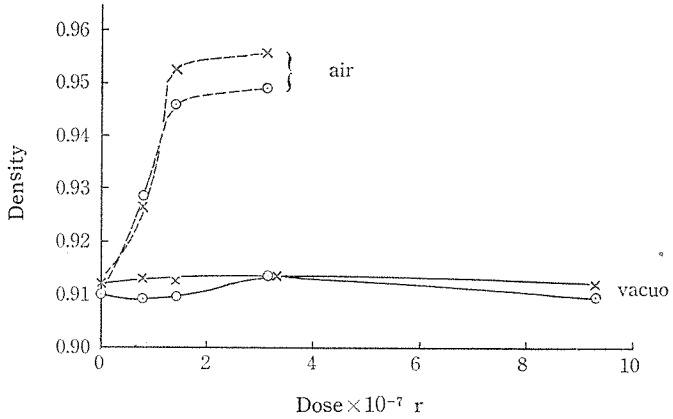

Fig. 1. Change in the density with dose. The values are given for unelongated (⊙) and elongated filaments (×).

3.2) Shrinkage by Heating

Percent shrinkage by heating was calculated from the change in length of the sample measured with a cathetometer. The specimens were 3 cm in length. The specimens were heated up at a constant rate of 1°C/min with a load of 50 mg for the sample irradiated in vacuo, and without a load for the samples irradiated in air, because the latter turned into more brittle at higher doses. The temperature dependence of shrinking of the irradiated filaments is given in Fig. 2.

The percent shrinkage of the sample irradiated *in vacuo* decreased regularly with radiation dose. When the irradiation was carried out in air, the unelongated filament increased in length at initial stage of heating, shrank at the temperature range of 130°C to 150°C, and flowed suddenly at a certain temperature. The unelongated filament irradiated at 3.1×10^{7}r in air, for example, flowed without shrinking.

On the other hand the elongated filament shrank gradually up to a temperature

and then flowed quickly. The changes of the flow point of these samples are shown in Fig. 3. The flow point of the filament irradiated *in vacuo* was lowered with increase in dose up to 3.1×10^7r and thereafter raised again. On the other hand, in the case of the filament irradiated in air the flow point was lowered considerably. The flow point for the unelongated samples appears to be higher than that for the elongated ones at the same radiation dose.

3. 3) Tensile Strength and Elongation at Break

Tensile properties were measured at 65% RH and 21°C by the use of an Instron Tensile Test Machine. The test specimen was 5 cm in length and stretched at a

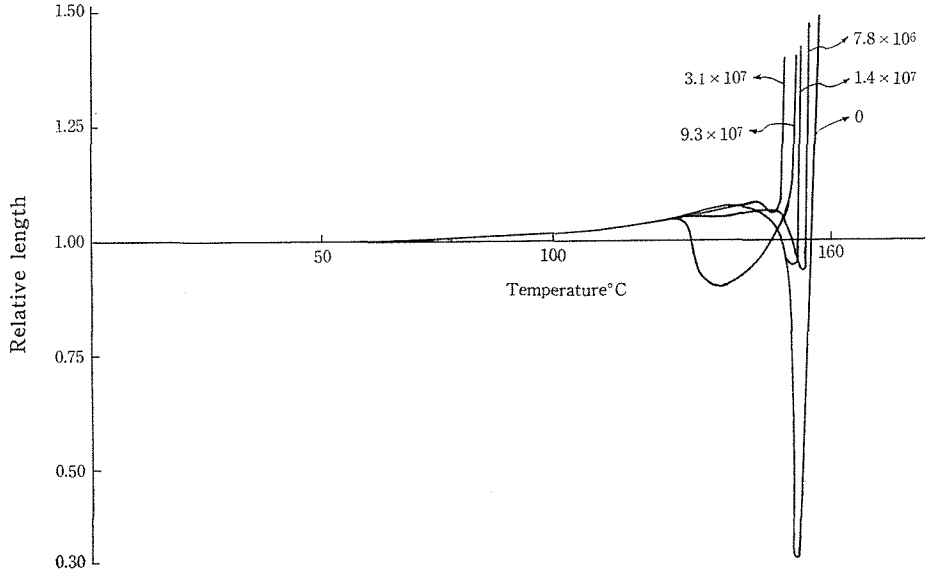

Fig. 2 (a). Variation of the percent shrinkage with temperature of unelongated filaments irradiated *in vacuo*.

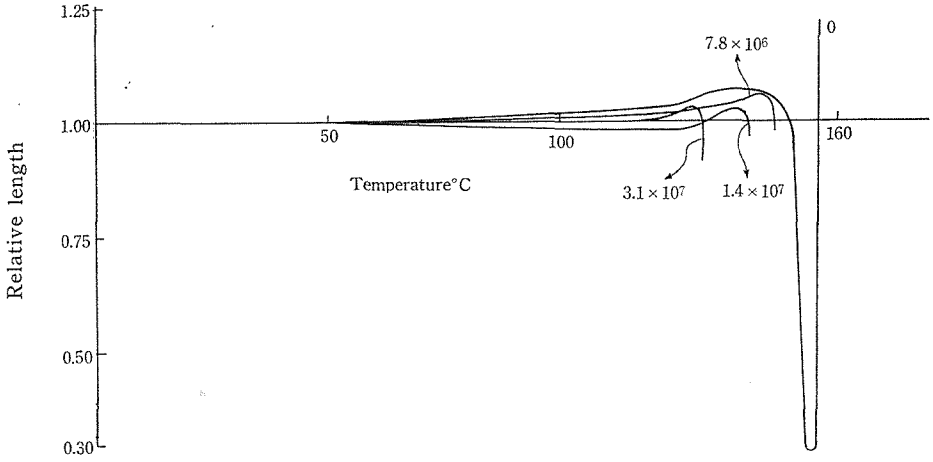

Fig. 2. (b). Variation of the percent shrinkage with temperature of unelongated filaments irradiated in air.

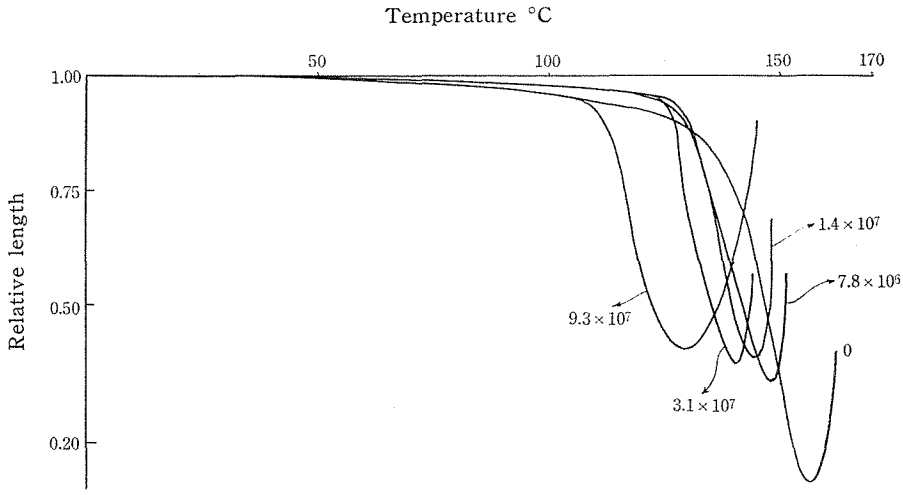

Fig. 2 (c). Variation of the percent shrinkage with temperature of elongated filaments irradiated *in vacuo.*

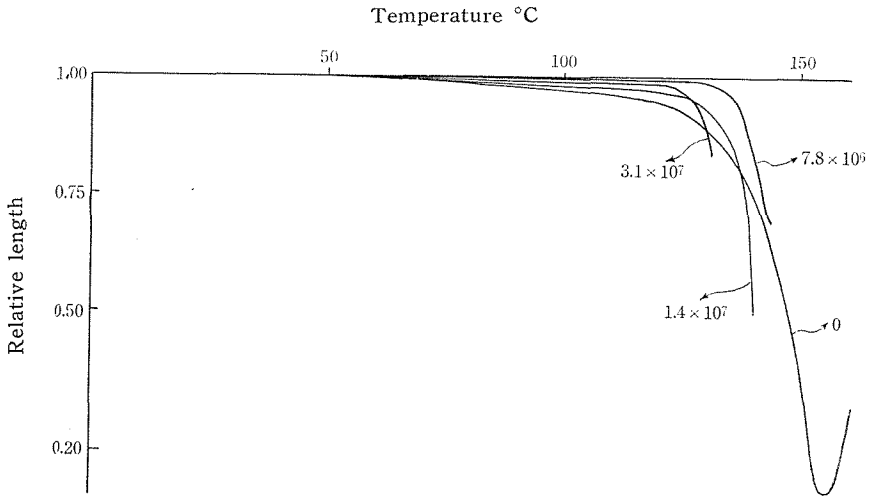

Fig. 2 (d). Variation of the percent shrinkage with temperature of elongated filaments irradiated in air.

rate of 2 cm/min. The changes in tensile strength and elongation at break with radiation dose are tabulated in Tables 1 and 2.

The tensile strength and elongation of the irradiated filaments were observed to decrease with radiation dose both *in vacuo* and in air. The tensile strength of the filament irradiated *in vacuo* decreased by some 30% to 40% at 1.4×10^7 r and thereafter remained almost constant up to 3.1×10^7 r. The decrease in these values of the filaments irradiated in air was larger than *in vacuo.* The unelongated samples irradiated at the dose above 1.4×10^7r and the elongated ones irradiated at above 3.1×10^7r could not be measured, because the samples became too brittle in the case of the irradiation in air.

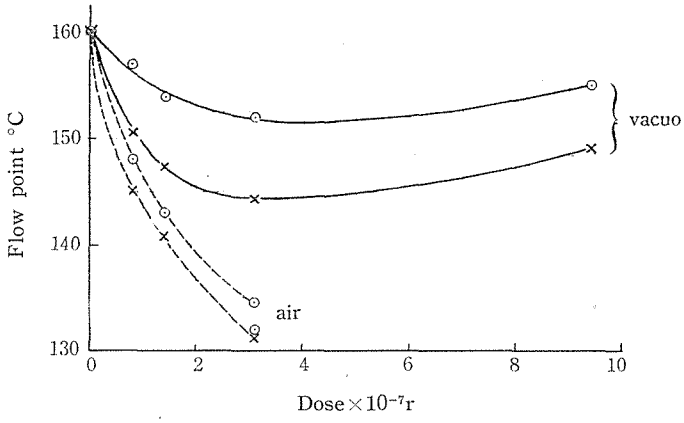

Fig. 3. Effect of atomosphere during irradiation on the flow point for unelongated (⊙) and elongated filaments (×).

Table 1. Tensile strength and elongation at break of the filament irradiated *in vacuo* at various radiation doses.

1) Unelongated filament

Dose r×10⁶	0	7.8	14	31	93
Denier	99	97	93	109	148
Tensile strength g/d	1.40	1.01	0.86	0.72	0.42
Relative tensile strength	1.00	0.72	0.61	0.51	0.30
Elongation %	540	448	377	384	43
Relative elongation	1.00	0.83	0.70	0.71	0.08

2) Elongated filament

Dose r×10⁶	0	7.8	14	31	93
Denier	20.9	19.6	19.8	18.2	21.5
Tensile strength g/d	7.48	5.48	4.49	4.63	2.83
Relative tensile strength	1.00	0.73	0.60	0.63	0.38
Elongation %	24	16	11	13	12
Relative elongation	1.00	0.68	0.45	0.53	0.49

Table 2. Tensile strength and elongation at break of the filament irradiated in air at various radiation doses.

1) Unelongated filament

Dose r×10⁶	0	2.1	7.8	14
Denier	99	84	102	—
Tensile strength g/d	1.40	1.10	0.44	—
Relative tensile strength	1.00	0.79	0.31	—
Elongation %	540	384	4	—
Relative elongation	1.00	0.71	0.06	—

2) Elongated filament

Dose $r \times 10^6$	0	2.1	7.8	14
Denier	20.9	21.1	20.3	23.4
Tensile strength g/d	7.48	5.06	2.01	0.83
Relative tensile strength	1.00	0.68	0.27	0.11
Elongation %	24	13	5	1
Relative elongation	1.00	0.55	0.19	0.05

3. 4) Stress-strain Curve

Stress-strain curves of the samples irradiated at various doses are shown in Fig. 4. With the unelongated filaments irradiated *in vacuo,* the shape of curves up to the yield point was independent of the radiation dose, whereas the resistance for stretching after yield point decreased with increase in dose.

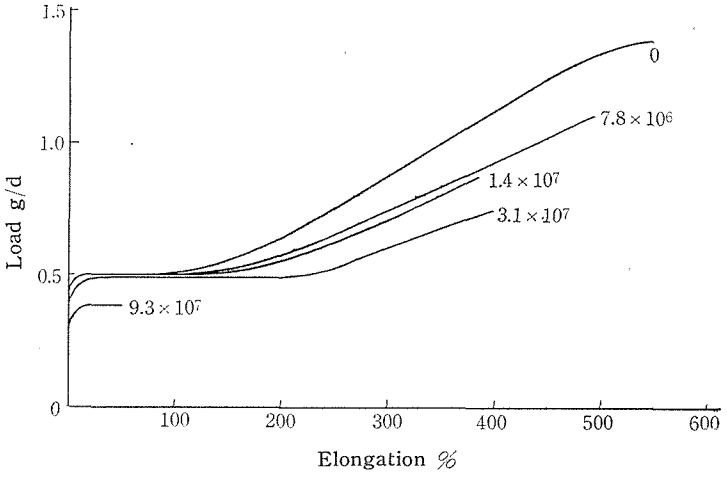

Fig. 4 (a). Load-elongation curves at various doses of unelongated filaments irradiated *in vacuo.*

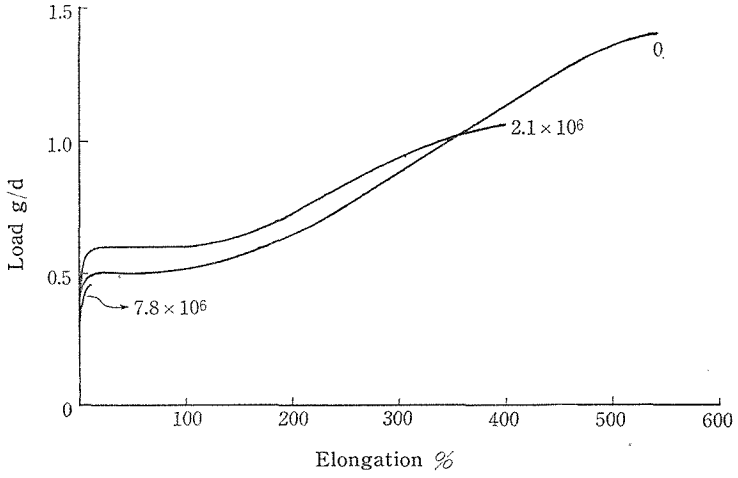

Fig. 4 (b). Load-elongation curves at various doses of unelongated filaments irradiated in air.

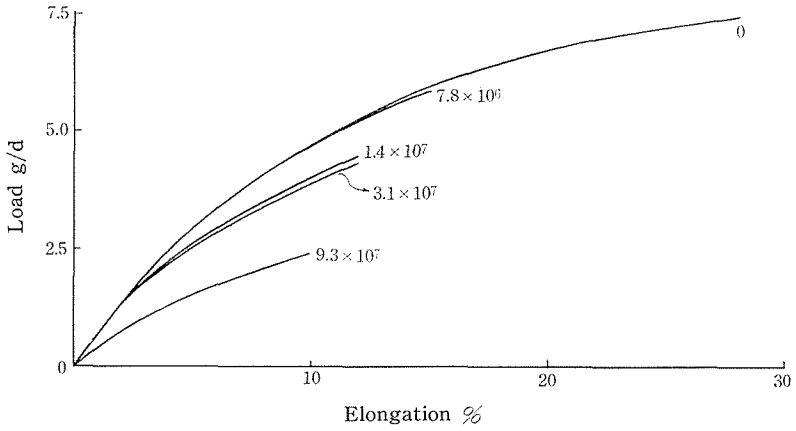

Fig. 4 (c). Load-elongation curves at various doses of elongated filaments irradiated *in vacuo*.

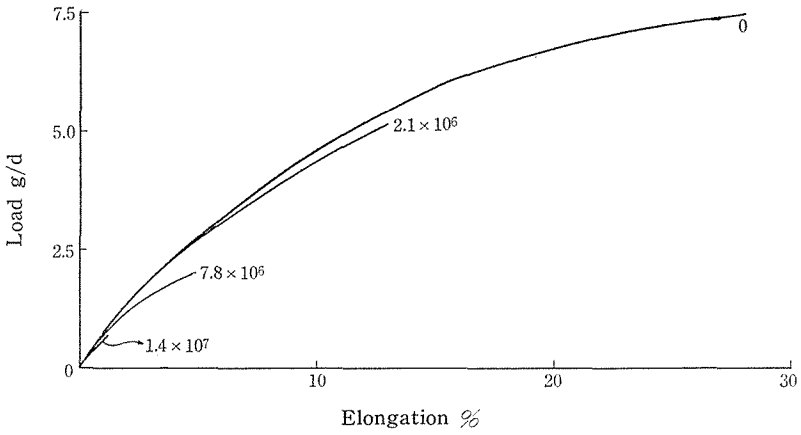

Fig. 4 (d). Load-elongation curves at various doses of elongated filaments irradiated in air.

The shape of curves of the elongated filaments irradiated *in vacuo* varied regularly with radiation dose. When the irradiation was performed in air, the load at the yield point of unelongated filaments did not change with radiation dose, except the result at a dose of 2.1×10^6r. The elongation decreased with increase in dose. The similar result was obtained on the elongated filament.

3.5) Young's Modulus

Young's moldulus was estimated at 1% elongation from the curves measured by the Instron Tensile Test Machine at 65% RH and 21°C. The specimen was 5 cm in length and stretched at a constant rate of 0.5 cm/min during each run. The results are listed in Table 3. Young's modulus did not change markedly except the elongated filament irradiated at 9.3×10^7r *in vacuo* and the unelongated one irradiated at 1.4×10^7r in air. However, the resistance for stretching decreased at higher stretchings within the radiation doses shown in the table.

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

1) Irradiation *in vacuo*

Dose r×10⁶	0	7.8	14	31	93
Unelongated filament	143	155	151	157	149
Elongated filament	729	756	680	709	494

2) Irradiation in air

Dose r×10⁶	2.1	7.8	14
Unelongated filament	151	279	—
Elongated filament	714	745	—

3.6) Elastic Recovery

Elastic recovery was measured using the Instron Tensile Test Machine at 65% RH and 21°C. The specimen was 5 cm in the initial length and stretched at a constant rate of 2 cm/min up to a given percentage of elongation. The elastic recovery was computed as the degree of recovery of stretching after removal of the given load and plotted against elongation in Fig. 5. The eleastic recovery was almost independent of the radiation dose both *in vacuo* and in air.

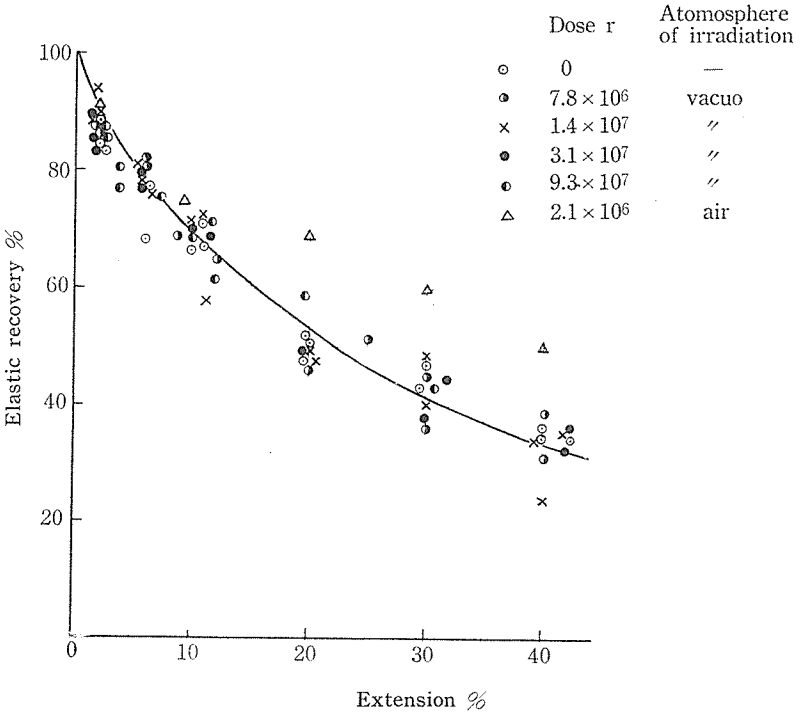

Fig. 5 (a). Elastic recovery of irradiated unelongated filaments.

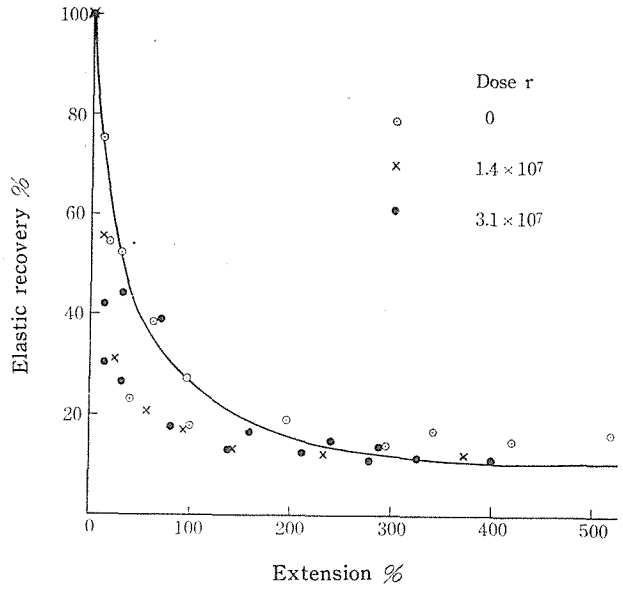

Fig. 5 (b). Elastic recovery of unelongated filaments irradiated *in vacuo*.

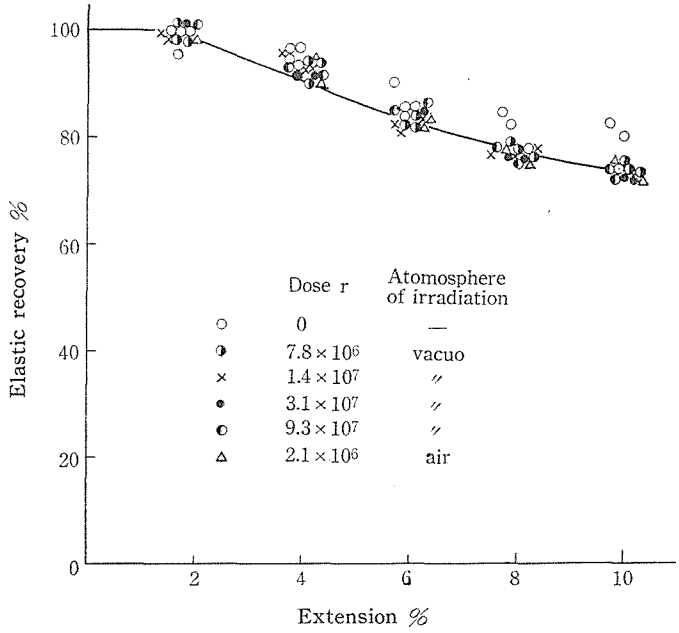

Fig. 5 (c). Elastic recovery of irradiated elongated filaments.

4. DISCUSSION

The density of the sample did not change with radiation *in vacuo*, but changed remarkably with radiation in air, just as that of the polyethylene reported previously. The considerable change in density by the irradiation in air may be ascribed to the changes in polymer structure due to oxydation occurred during irradiation, and this may be interpreted as an evidence that oxygen reacts on free radicals

very easily. The variation in shrinking can be accounted for the decrease of interaction between molecules by degradation at the initial stage of the irradiation and, in addition, for the decrease of mobility of molecules by the competitive reaction of crosslinking and degradation at higher doses. The sharp lowering of the flow temperature with dose may possibly be explained similarly, so far as the effect of oxygen is concerned. From the result that the polypropylene crosslinks at the radiation doses of 2×10^7r to 5×10^7r the behavior, that the flow point of the filament irradiated *in vacuo* decreased at the doses up to 3.1×10^7r and then began to increase at higher doses, seems to be reasonable. The flow points of the unelongated samples were higher than those of the elongated ones at the same dose. Dependence of the flow point on orientation had been found in the case of high density polyethylene. It is hard to see whether the degree of orientation has an effect on the flow point data or not, considering the difference of surface area of the filament. The changes in tensile strength can be interpreted also as due to the decerase in molecular weight by irradiation. And the decrease in tensile strength was accelerated by the presence of oxygen. When the irradiation was carried out *in vacuo*, the tensile strength remained nearly constant over the radiation dose range of 1.4×10^7r to 3.1×10^7r. Such a tendency may be attributed to crosslinking as is seen about the flow point.

Young's modulus and the elastic recovery of the samples were almost unchanged with dose, in spite of the change in density, flow point and tensile strength which are responsible to the changes in chemical structure of the polymer. It is interesting that Young's modulus is independent of dose, while the resistance for stretching after yield point depends on the dose. But these properties may change with dose at higher temperatures.

The variation in mechanical properties of the filament with the degree of elonga tion was known to be independent of the radiation doses. The result on density is approximately in agreement with the result reported by Sofue, Tabata and Tajima[7], but on the tensile strength is not; it was not found in our present work that the tensile strength of the sample irradiated *in vacuo* increased by about 15% at the doses up to 1×10^8r. Effect of irradiation temperature on the properties of polypropylene filament is to be treated in a following paper.

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