

PROTON IRRADIATION EFFECTS ON ORGANIC POLYMERS

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Summary

Organic polymer films (100 μm thickness) of polyethylene, polypropylene, polyethyleneterephthalate, and polyethersulfone were irradiated by protons of 8 MeV using a cyclotron, and their radiation effects were investigated by the changes of mechanical properties. In order to irradiate protons uniformly over wide area of polymer films, specimens were scanned during proton irradiation using a special apparatus. The absorbed dose was measured by CTA and RCD film dosimeters, and can be determined that 1 $\mu\text{C}/\text{cm}^2$ of 8 MeV proton fluence is equivalent to 54 kGy. For polyethylene and polypropylene, there was no significant difference between proton and electron irradiation for same doses. However, for polyethersulfone the decay of mechanical property was observed to be less than that of irradiation by electron.

Introduction

Organic polymers are used as the materials of components and equipments in nuclear facilities such as nuclear power plants, fuel reprocessing, and waste storage, and in artificial satellites in space. They would be subjected to high energy radiations of γ -rays, electrons, neutrons, and protons in their environments to result in decay of their properties. Although the radiation resistance of polymers against γ -rays or electrons has been well investigated by many researchers, the studies against neutrons and ions are very scarce except the basic researches such as free radical behavior by ESR and molecular weight changes.

The linear energy transfer (LET) of neutron or proton in organic polymer materials is very different from LET of γ -ray or electron, so the irradiation effects are expected to be different between them. In fact, some of basic researchers reported the differences^{1,2}, but others observed no difference³.

In this study, proton irradiation effects on the typical organic polymers were investigated by the measurements of mechanical properties from the view point of the practical usage as materials, and compared with the effect by γ -ray or electron irradiation of polymers. For this purpose, we constructed the special irradiation apparatus which can irradiate protons uniformly over the wide area of polymer specimens. Generally, the organic polymers are more sensitive to irradiation, and have less thermal resistance and a small thermal conductivity

than inorganic materials, so if the protons were irradiated by proton beam as like a irradiation to inorganic materials, the specimens would be melted and evaporated by the heat given by proton irradiation. Then, the proton irradiation flux must be controlled so that the temperature of specimens does not exceed a certain value. For the measurements of mechanical properties, a number of specimens are needed to be irradiated uniformly for one kind of polymer.

Using a newly constructed irradiation apparatus, the above problems could be overcome.

Experimental

Samples were the aliphatic polymers of polyethylene (PE) and polypropylene (PP), and aromatic polymers of polyethyleneterephthalate (PET) and polyethersulfone (PES). Their chemical structure were shown in table 1. All samples were films with about 100 μm thickness.

Proton was irradiated to polymer films under vacuum at room temperature using a cyclotron in RIKEN. The energy of proton was selected to 5, 8, and 15 MeV, and the beam current was 0.1 - 1 μA on specimens. The beam was defocused and cut to the size of 5 mm x 20 mm or 5 mm x 10 mm. The specimen was lapped on the aluminum rotor with a diameter of 50 mm and length of 130 mm as seen in Fig.1. The rotor was rotated and simultaneously moved along the rotation axis repeatedly during proton irradiation. Using the apparatus, the specimens could be irradiated uniformly in the area of about 150 mm x 30 mm with two stages of different exposure, which had enough dimensions for the measurement of the mechanical properties. Irradiation time was 1 - 30 min for one specimen, and the temperature of specimen was estimated to be maintained below 60°C at the end of irradiation for 30 min. The thermal effect during irradiation could be neglected.

The proton beam current passed through specimen was monitored and the total fluence was measured during irradiation for each specimen. The absorbed energy (dose) in a specimen was determined by comparing with the film dosimeter irradiated in the same condition. The film dosimeters were CTA (cellulose triacetate containing specific dye)⁴ and RCD (Radiachromic dye dosimeter)⁵ which are well used in γ -ray and electron dosimeters.

Electron irradiation was carried out for the comparison with proton irradiation. The electron energy was 2 MeV and the current was about $1 \mu\text{A}/\text{cm}^2$.

The mechanical properties of irradiated specimens was measured by tensile testing, and obtained the elongation and tensile strength at break.

Table 1. Chemical structure of organic polymers

Polyethylene	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ (-\text{C}-\text{C}-\text{C}-\text{C}-) & & & \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}_n$
Polypropylene	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ (-\text{C}-\text{C}-\text{C}-\text{C}-) & & & \\ & & & \\ \text{H}_3\text{C} & \text{H} & \text{CH}_3 & \text{H} \end{array}_n$
Polyethylene-terephthalate	$\begin{array}{cccc} \text{H} & \text{H} & \text{O} & \text{O} \\ & & & \\ (-\text{C}-\text{C}-\text{O}-\text{C} & \text{C}_6\text{H}_4 & -\text{C}-\text{O}-) & \\ & & & \\ \text{H} & \text{H} & & \end{array}_n$
Polyethersulfone	$\begin{array}{c} \text{O} \\ \\ (-\text{C}_6\text{H}_4-\text{S}-\text{C}_6\text{H}_4-\text{O}-) \\ \\ \text{O} \end{array}_n$

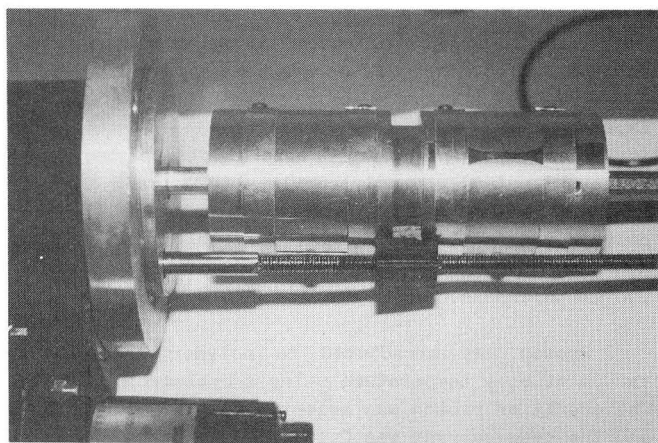


Fig.1 Apparatus for proton irradiation over wide area of polymer films

Results and Discussion

1. Determination of Dose

When the CTA film dosimeter with $125 \mu\text{m}$ thickness was irradiated by 8 MeV protons at a condition with beam current of $0.4 \mu\text{A}$, rotor rotation speed of 120 rpm, and moving rate of 30 mm/min, the distribution of dose was examined by measurements of photoabsorption through the dosimeter using a microphotometer at 280 nm. The changes of optical density, which is proportional to dose, was nearly constant over the film within the accuracy of the dosimeter, that is, the proton was irradiated uniformly on the film.

Fig.2 shows the relation between the changes of optical density and proton fluence of incidence in the area of film when the CTA dosimeter was irradiated by 8 MeV proton up to $80 \mu\text{C}$ in 56cm^2 area. The ΔOD increases linearly with increase of fluence. In the study by electron irradiation, the ΔOD is proportional to dose and the relations are determined as

$$0.54 \text{ of } \Delta\text{OD} = 100 \text{ kGy} \quad (1)$$

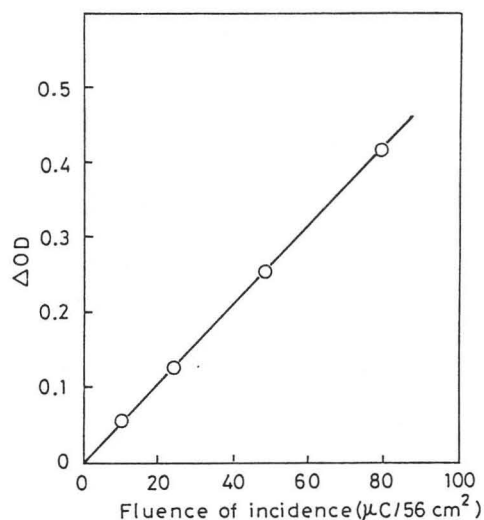


Fig.2 Changes of optical density vs. proton fluence in CTA film dosimeter

Fig.3 shows the dose at depth in CTA dosimeter when a stack of CTA films of $125 \mu\text{m}$ was irradiated by 8 MeV proton. This figure means that the proton can penetrate through 5 pieces of CTA films from the incidence and stop at the 6th. By change of proton incidence energy, the depth-dose relation showed another one as reported by Sunaga et al..

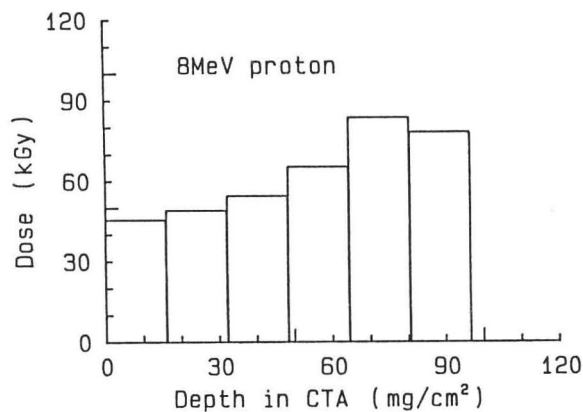


Fig.3 Depth dose in CTA film dosimeter irradiated by 8 MeV proton.

In a case that the specimen is enough thin as compared with the range of proton penetration as seen in Fig.3, the dose in the dosimeter can be expressed in eq.(2).

$$D = S Q \quad (2)$$

where D is dose in kGy, S is stopping power in $\text{MeV}/\text{g}_2\text{cm}^2$, and Q is proton fluence of incidence in $\mu\text{C}/\text{cm}^2$.

From eq.(1) and Fig.2, $1 \mu\text{C}/\text{cm}^2$ corresponds to 54 kGy. Then, the S in eq.(2) can be derived to $53.9 \text{ MeV}/\text{g}_2\text{cm}^2$ at 8 MeV of proton energy. The other hand the calculated stopping power of CTA at 8 MeV energy is $51.8 \text{ MeV}/\text{g}_2\text{cm}^2$, and agrees well with the observed value. Then, the fluence of proton with 8 MeV energy was determined,

$$1 \mu\text{C}/\text{cm}^2 = 54 \text{ kGy} \quad (3)$$

The sensitivity of CTA dosimeter was investigated by Sunaga et al., and they reported that there are no energy dependence from 8 to 15 MeV in their experimental conditions.

In case of RCD dosimeter, the observed values by proton irradiation was compared with that of electron irradiation, and the result was principally the same with that of CTA. As the RCD dosimeter was very thin, the treatments was not so easy comparing with CTA dosimeter, so we used mainly the CTA dosimeter. The application of RCD dosimeter for proton and other heavy ions had been well studied by Hansen et al., and they reported that the sensitivity of RCD is the same among ^{60}Co γ -ray, 10 MeV electron, and 10 - 16 MeV proton. Both of CTA and RCD are composed of organic polymers, and the sensitivity depends on the energy absorption in polymer matrix, then these dosimeter would reflect well the dose in organic polymers.

2. Proton Irradiation Effects on Organic Polymers

For the aliphatic polymers of polyethylene and polypropylene films irradiated by protons of 8 MeV, the elongation at break by tensile testing was plotted against the fluence of proton in Fig.4-a for PE and Fig.5-a for PP. If the absorbed dose by proton is corrected by relation of eq.(3), the elongation vs. dose is shown in Figs.4-b and 5-b for PE and PP, respectively. In case of electron irradiation, the elongation vs. fluence and dose is shown in the same

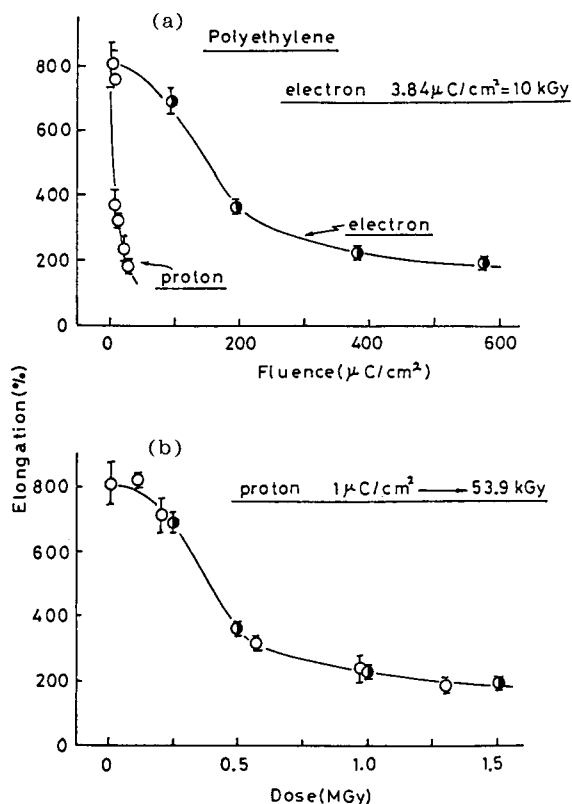


Fig.4 Elongation at break against fluence and dose for polyethylene films irradiated by electron and proton

figures for respective polymers for the comparison with the proton irradiation. The change of elongation which reflects well the decay of mechanical properties of PE and PP indicates that there is no significant difference between proton and electron irradiation. The other mechanical properties of tensile strength and modulus against dose were also the same changes for proton and electron. So far as the changes of mechanical properties for aliphatic polymers of PE and PP, the irradiation effects by proton seems to be the same with those by electron.

For polyethyleneterephthalate(PET) films irradiated by proton and electron, the tensile strength and elongation at break are plotted against dose in Fig.6. The dose by proton irradiation was also corrected with eq.(3). The changes of elongation show the same behaviour between proton and electron, but the changes of tensile strength show a some difference, that is, the decay by proton irradiation is less than that by electron irradiation.

In Fig.7, the tensile strength and elongation at break are plotted against dose when polyethersulfone(PES) film was irradiated by proton and electron with the same conditions as PET films. This shows a certain difference between proton and electron in both of tensile strength and elongation though the experimental data were scattered. These observed data mean that the degradation by proton is less than that by electron irradiation. At present, it is suspected that these differences are substantial

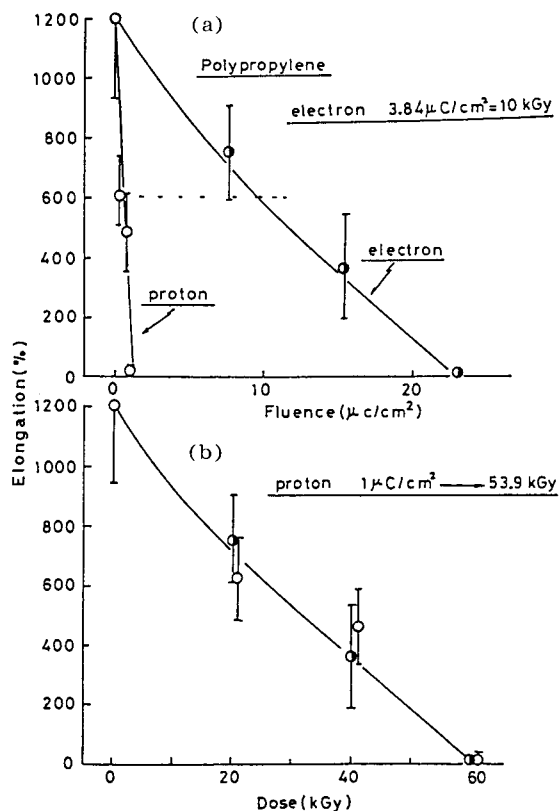


Fig.5 Elongation at break against fluence and dose for polypropylene(PP) films irradiated by electron and proton.

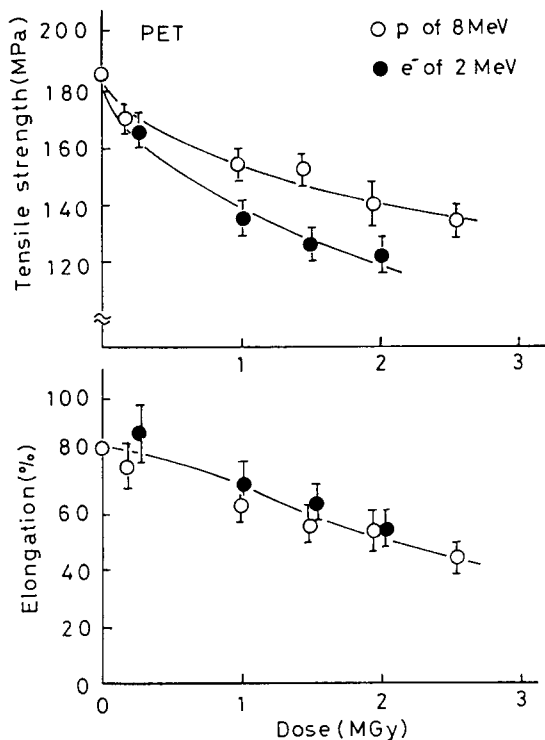


Fig.6 Tensile strength and elongation at break against dose for polyethyleneterephthalate(PET) irradiated by proton and electron.

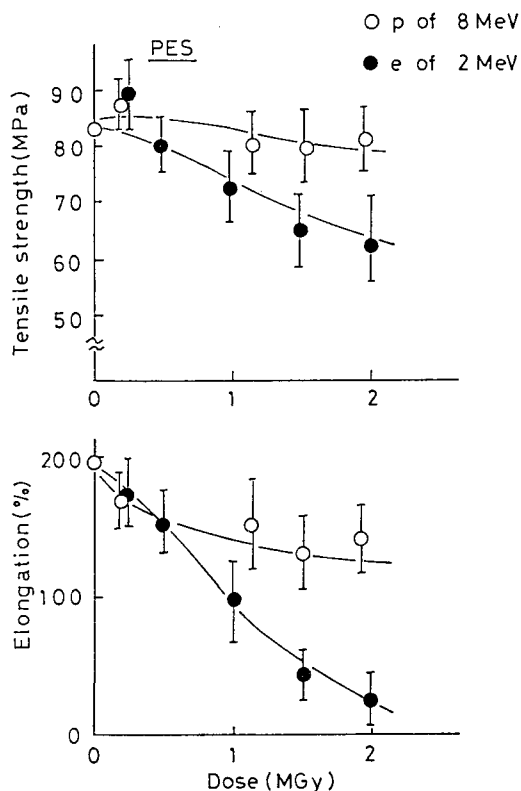


Fig.7 Tensile strength and elongation at break against dose for polyethersulfone(PES) irradiated by proton and electron

in irradiation effects, because they come from experimental procedures of irradiation or testing. For this sample, it needs more precise experiments. However, for PET sample a some difference was observed in tensile strength, so the aromatic polymers might be different between proton and electron.

The mechanical properties of polymer materials are related to the intrinsic polymer chain properties, chain length or molecular weight, and chain entanglements such as physical or chemical bonding. The radiation effects on the mechanical property should be mainly originated from the chain scission and crosslinking of polymer chains through the chemical processes as excitation, ionization, free radical formation, and reactions of active species.

For aliphatic polymers of PE and PP, the fact that there is no difference in mechanical property between proton and electron suggests that the probability of crosslinking and/or chain scission of polymer chains would be the same, even if the chemical process might be different between proton and electron depending on their LET.

For aromatic polymer as PES, these characteristics of chemical process might reflect on the final products of crosslinking and/or chain scission which control mechanical property. Even if these models were accepted, it would be difficult to explain the reason why the degradation by proton is less than that by electron.

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