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High energy ion irradiation effects on polymer materials: 2. Proton irradiation effects on PMMA and GFRP

H. Kudoh*, T. Sasuga and T. Seguchi
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma, 370–12 Japan

and Y. Katsumura
The University of Tokyo, Faculty of Engineering, Department of Quantum Engineering and System Science, Hongo, Bunkyo-ku, Tokyo, 113 Japan
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The changes in mechanical properties of poly(methyl methacrylate) (PMMA) and glass fibre reinforced plastic (GFRP) induced by high energy (30, 45 MeV) protons were studied and compared with those induced by Co-60 gamma rays. The flexural strength at break of PMMA and GFRP showed the same degradation behaviour as a function of dose, indicating no difference between proton and Co-60 gamma ray irradiation.

(Keywords: ion; gamma irradiation; mechanical properties)

INTRODUCTION

Fusion reactors require polymer and fibre reinforced plastic as electric insulators, where the materials are subjected to high energy neutron irradiation at very low temperature. The radiation resistance of materials at low temperature has been investigated by the authors using gamma rays[1,2]. The radiation damage to polymers by neutron irradiation is mainly due to the recoiled protons (H atoms) from the polymer itself, and so the irradiation effects of neutrons can be simulated by proton irradiation. Knowledge about the degradation of polymers induced by ions such as protons is essential. The radiation resistance of polymeric materials has been studied extensively with gamma rays or electron beams in terms of changes in mechanical properties such as tensile elongation and flexural strength[3]. The radiation effects have been assumed to be different between ions and gamma rays or electron beams due to the difference in linear energy transfer (LET). The evaluation of radiation resistance of polymers to ions is necessary, but it requires irradiation over a wide area with a uniform dose to measure the mechanical properties accurately. There are few facilities for this and few reports[4,5]. For this reason, ion accelerators and an ion irradiation chamber for uniform irradiation[6,7] were prepared at the Japan Atomic Energy Research Institute (JAERI), the Takasaki Radiation Chemistry Research Establishment (TRCRE), called TIARA (Takasaki Ion Accelerators for advanced Radiation Application). The authors have studied high energy proton irradiation effects for several polymers and compared the results with those of electron irradiation in previous reports[7–9]. A LET effect was hardly observed for the tensile test of PE (polyethylene) and PTFE (polytetrafluoroethylene), whereas LET effect was observed for PES (polyethersulfone) and UPS (bisphenol A type polysulfone). It should be pointed out that whether an LET effect appears or not depends on the 'aromaticity' of the polymers[4,5]. In this work, the changes in flexural strength induced by proton irradiation for PMMA (poly(methyl methacrylate)) and GFRP (glass fiber reinforced plastic; glass/diglycidyl ether of bisphenol-A type epoxy resin hardened with dicyano diamide) were studied and compared with those of Co-60 gamma ray irradiation.

* To whom correspondence should be addressed

EXPERIMENTAL

Materials

Commercial specimens of PMMA (3 mm thick) and of GFRP (2 mm thick), respectively, were used for flexural test.

Irradiation

A proton spot beam of 10 mm diameter from the Cyclotron accelerator was scanned uniformly over a 100 × 100 mm wide area. Ion energy was selected (30 and 45 MeV for PMMA and 30 MeV for GFRP, respectively), so that protons pass through the materials, and to reduce the induced radioactivity from the glass in GFRP. The materials were put on a water cooled holder and irradiated at room temperature under vacuum. The ion current was 200–300 nA to avoid abrupt gas

Table 1 Irradiated ions, stopping power (MeV cm^2 g^{-1}) and ion penetration range (mm)[a]

Polymer	Ion	Stopping power (MeV cm^2 g^{-1})	Range (mm)	Current (nA cm^{-2})	Dose rate (Gy s^{-1})
PMMA	45 MeV H^+	11.5	19.2	2–3	38.4–57.6
	30 MeV H^+	16.3	9.02	2–3	32.6–48.9
GFRP	30 MeV H^+	16.1[b]	7.84[b]	2–3	32.2–48.3

[a] All irradiations were carried out under vacuum at room temperature
[b] Values for CTA (cellulose triacetate)

evolution that deteriorates the vacuum in the chamber and accelerator. The absorbed dose was calculated as the product of fluence and Bethe's mass stopping power. A cellulose triacetate (CTA) film dosimeter was used for determination of the dose in the polymer prior to irradiation of PMMA and GFRP, and good agreement between the observed dose and expected dose was obtained. The stopping powers, ranges and irradiation conditions are shown in *Table 1* (in *Table 1*, the data for CTA are substituted for those for GFRP, because the content of GFRP is so complex). The details of the proton irradiation procedure are reported elsewhere[6,7]. For comparison with the effect by proton irradiation, Co-60 gamma ray irradiation was performed in a nitrogen gas atmosphere at room temperature at a dose rate of 8 kGy h^{-1}.

Measurement

Three-point flexural tests were carried out at room temperature using an Instron 4301 tensile testing machine. The molecular weight of PMMA was measured by g.p.c. (gel permeation chromatography, Tosoh Co. Ltd, HLC-8020). The measurements were carried out at 40°C using $CHCl_3$ as solvent. The glass transition temperature (T_g) of GFRP was measured by d.s.c. (differential scanning calorimetry, Perkin Elmer DSC 7) at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

PMMA

Figure 1 shows the change in flexural strength of PMMA measured at RT as a function of absorbed dose. The flexural strength is about 130 MPa initially, and decreases with dose above 0.1 MGy. The strength decreases to half of the initial value at around 150 kGy. The behaviour is the same for gamma rays, 45 and 30 MeV protons. *Figure 2* shows the change in molecular

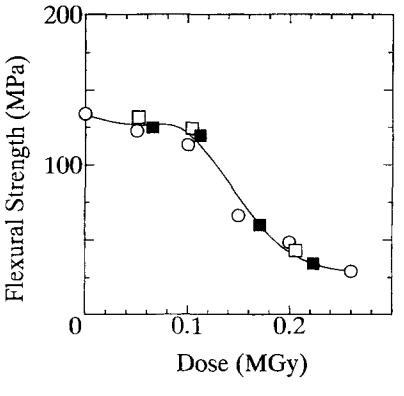

Figure 1 Flexural strength of PMMA (O, gamma ray; □, 45 MeV proton; ■, 30 MeV proton)

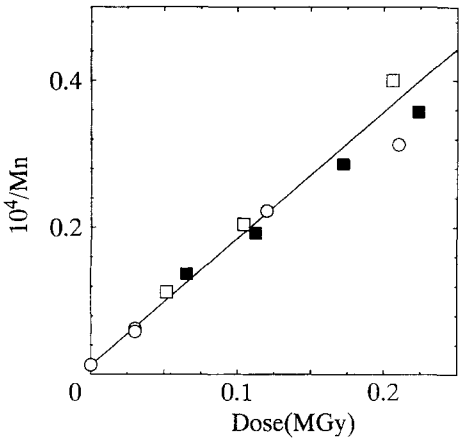

Figure 2 Number average molecular weight (M_n) of PMMA (O, gamma ray; □, 45 MeV proton; ■, 30 MeV proton)

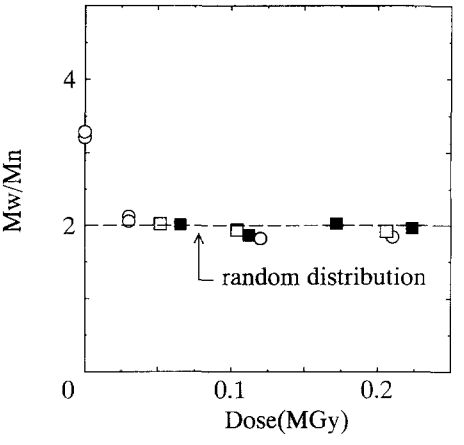

Figure 3 The ratio of weight average molecular weight to number average molecular weight, M_w/M_n of PMMA (O, gamma ray; □, 45 MeV proton; ■, 30 MeV proton)

weight (M_n) as a function of absorbed dose. The M_n decreases in the same way for gamma rays, 45 and 30 MeV proton irradiations. *Figure 3* shows the ratio of weight average to number average molecular weight, M_w/M_n. It is about 3 before irradiation and around 2 after a small dose, which means that the molecular weight distribution is most probable. The G value of chain scission of PMMA calculated from *Figure 2* is 1.7, which agrees well with values in the literature[10]. The experimental results of flexural strength, M_n and M_w/M_n indicate that the chain scission takes place in the same way in number and spatial distribution for irradiations of gamma rays and 45 and 30 MeV protons, and that the decrease in mechanical properties depends only on the dose. An LET effect on PMMA degradation is not observed in the LET range of our experiments

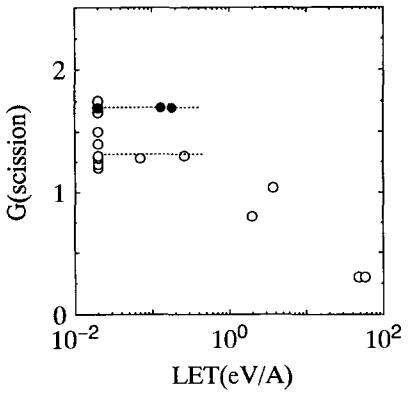

Figure 4 *G* (scisson) for PMMA as a function of LET (○, reported values taken from ref. 10; ●, this work)

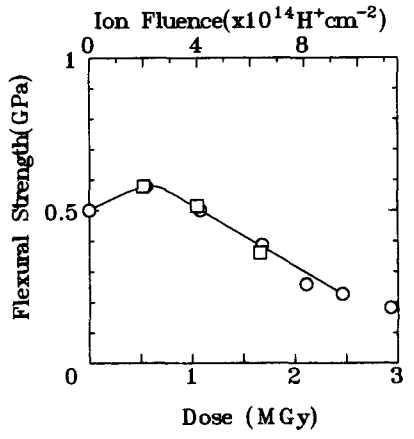

Figure 5 Flexural strength of GFRP (○, gamma ray; □, 30 MeV proton)

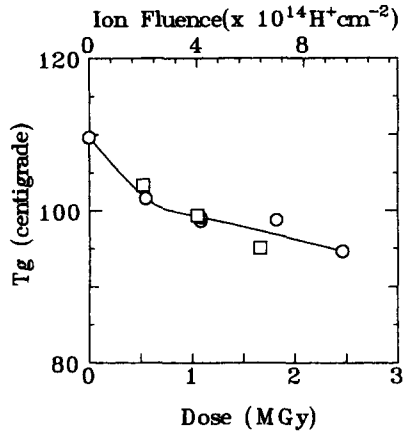

Figure 6 Glass transition temperature (T_g) of GFRP (○, gamma ray; □, 30 MeV proton)

(1.8–16 eV cm^2 g^{-1}). On the other hand, Yates and Shinozaki[10], and Schnabel and Klaumunzer[11] reported that the *G* value of scission of PMMA decreases with increasing LET. However, as *Figure 4* shows, the value of *G* (scission) as a function of LET seems to be constant within a certain LET range (up to *ca* 0.5 eVA^{-1}), while the *G* value for gamma ray irradiation scatters depending on the authors, pre-treatment conditions, and other factors.

GFRP

Figure 5 shows the change in flexural strength of GFRP measured at RT as a function of absorbed dose. The strength at 0.5 MGy increased about 20% to 0.6 MPa from the initial value of 0.5 MPa, and decreased with dose above 1 MGy. The behaviour of flexural strength vs dose is the same for 30 MeV protons and gamma rays. The radiation degradation of GFRP is attributed to the degradation of matrix resin. *Figure 6* shows the change in glass transition temperature, T_g, of epoxy resin, determined by d.s.c. T_g is about 110°C initially, and decreases with dose. The decrease of T_g indicates the degradation of the network structure of the epoxy resin. The scission probability of epoxy resin is the same for gamma rays and 30 MeV protons. We have already carried out irradiation of 45 MeV protons on carbon fibre reinforced plastic (CFRP; CF/polyimide, CF/epoxy)[12]. That work also showed no difference in the behaviour of flexural strength as a function of dose for 45 MeV protons and 2 MeV electrons, though the dose range was not so high as to cause degradation in flexural strength. Considering these results, there seems to be little or no LET effect within the LET range in this work. Our previous work[4,5] implies that the absence or presence of an LET effect is related to the aromatic character of the target materials. Though the matrix resins of these FRPs contain aromatic compounds, the LET of 30 and 45 MeV protons would be sufficiently small to bring about a LET effect.

CONCLUSION

High energy ion irradiation effects on PMMA and GFRP were studied by changes in flexural strength, molecular weight and glass transition temperature. They showed the same behaviour with respect to absorbed dose for proton and Co-60 gamma ray irradiation, which means that the LET effects on the degradation of these polymers are very small within the LET range in this work.

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