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High energy ion irradiation effects on polymer material: 4. Heavier ion irradiation effects on mechanical properties of PE and PTFE

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The changes in mechanical properties of polyethylene (medium density, MDPE) and poly(tetrafluoroethylene) (PTFE) induced by heavier ions such as He^{2+} 20 MeV, C^{5+} 220 MeV and O^{5+} 100 MeV ions were studied and compared with those induced by 2 MeV electrons. The changes in elongation at break were similar for exposures to the heavier ions and for 2 MeV electron irradiations. The mechanical properties of the two polymers therefore seem to have little LET dependence. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ion irradiation effects; mechanical property; LET)

Introduction

Polymeric materials are used for space and fusion reactor applications (e.g. as construction materials and electric insulators), where the materials are subjected to high energy ions and/or neutron rays. To help select materials for such applications, the authors have been studying ion irradiation effects on polymeric materials. In our previous reports, we have studied high energy proton (10–45 MeV) irradiation effects for several polymers and compared these with electron beam and Co-60 gamma ray irradiations. We concluded that LET (Linear Energy Transfer) effects are minor for tensile properties of PE (polyethylene) and PTFE (polytetrafluoroethylene)[1,2], and for flexural properties for PMMA (poly(methyl methacrylate)), GFRP (glass fibre reinforced plastic, epoxy resin)[3,4] and CFRP (carbon fibre reinforced epoxy resin and carbon fibre reinforced polyimide)[5]. On the other hand, LET effects were observed for PES (polyethersulfone) and UPS (bis-phenol A type polysulfone)[1,2,6,7]. We proposed the existence of a threshold LET, above which the LET effect appears[8]. We hypothesized that the threshold of LET is smaller for UPS and PES than for other materials because of such factors as aromaticity and the thermalizing process of the ejected electrons. If PE, PTFE, etc. are exposed to sufficiently high LET radiation, we would expect them to show an LET effect even though PE and PTFE do not show a clear LET effect for protons in terms of mechanical property changes. In this work, changes in tensile elongation at break induced by heavier ion irradiations (He^{2+} 20 MeV, C^{5+} 220 MeV and O^{5+} 100 MeV) for PE and PTFE are reported and compared with those caused by 2 MeV electron beam irradiation.

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Experimental

The experimental procedures have been described previously[1,2,9]. The materials studied are medium density polyethylene (MDPE) of 0.2 mm thickness, and polytetrafluoroethylene (PTFE) of 0.1 mm thickness. Samples were placed on a water-cooled holder and irradiated at room temperature under vacuum by using a Cyclotron accelerator. An ion spot beam of 10 mm diameter was scanned uniformly over a 100 mm × 100 mm area. Ions and energies used were He^{2+} 20 MeV, C^{5+} 220 MeV and O^{5+} 100 MeV for MDPE and H^{+} 45 MeV, D^{+} 10 MeV, He^{2+} 50 MeV, He^{2+} 20 MeV, C^{5+} 220 MeV and O^{5+} 100 MeV for PTFE. Except for O^{5+} 100 MeV, the absorbed dose was calculated as the product of fluence and the average LET inside the specimens. The range of O^{5+} 100 MeV ions is smaller than the thickness of the specimens, so the dose was calculated as the total energy deposited in the specimens, that is, (fluence) × (energy)/(thickness × density). The LET and ranges calculated[10] are shown in *Table 1* with the average LET for O^{5+} 100 MeV ions. For comparison purposes, 2 MeV electron beam irradiation was also performed. Tensile tests were carried out at room temperature using an Instron 4301 tensile testing machine.

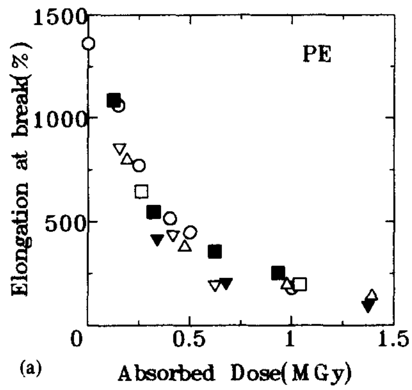
Results and discussion

Irradiation effects on the mechanical properties of PE. *Figure 1* shows the change in elongation and tensile strength at break of MDPE as a function of absorbed dose. The elongation at break of MDPE was about 1300% initially and decreased with dose, reaching half of the initial reading at around 0.3 MGy. Tensile strength was about 32 MPa initially and decreased to a minimum of around 22 MPa after 0.3 MGy. This was followed by a gradual increase with further dosage, indicating that

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

Polymer	Ion	Range (mm)	LET ($MeV\,cm^2\,g^{-1}$)		
			Initial	Final	Average
PE	He^{2+} 50 MeV	1.78	168.6	178.8	173.7
(200 μm)	He^{2+} 20 MeV	0.345	353.9	530.6	442.3
	C^{5+} 220 MeV	1.22	1098	1188	1143
	O^{5+} 100 MeV	0.158	4396	–	6805[a]
PTFE	He^{2+} 50 MeV	1.01	126.6	186.7	156.7
(100 μm)	He^{2+} 20 MeV	0.202	262.7	361.6	312.2
	C^{5+} 220 MeV	0.658	846.6	912.4	879.5
	O^{5+} 100 MeV	0.090	3348	–	4936[a]

[a] Energy/range/density



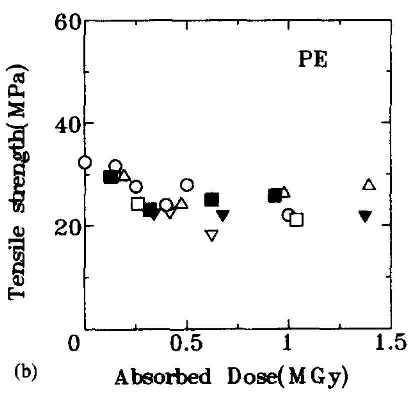


Figure 1 (a) Elongation at break of PE. (b) Tensile strength of PE irradiated with: ■, He^{2+} 50 MeV; □, He^{2+} 20 MeV; ▽, C^{5+} 220 MeV; ▼, O^{5+} 100 MeV, respectively. ○, 2 MeV electron under vacuum; △, H^+ 10 MeV

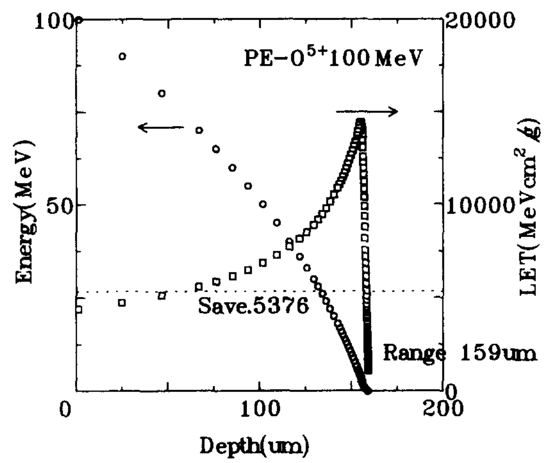


Figure 2 Energy and LET as a function of depth in PE for O^{5+} 100 MeV. Save. means the average deposited energy per unit thickness for whole materials, that is, ion energy/sample thickness/density

crosslinking dominates scission in the later stages. The degradation behaviour vs absorbed dose appears to be independent of the irradiation conditions even though the LET varies by a factor of *ca.* 3000 from the 2 MeV electron beam (1.77 $MeV\,cm^2\,g^{-1}$) to the C^{5+} 220 MeV ions (1143 $MeV\,cm^2\,g^{-1}$, on average) or O^{5+} 100 MeV ions (5376 $MeV\,cm^2\,g^{-1}$, on average). Moreover, while the C^{5+} 220 MeV ions give almost homogeneous energy deposition, that is, the ratio of the LET at the incoming surface (minimum) to the LET at the outgoing surface (maximum) is 1.08, the O^{5+} 100 MeV ions give a very inhomogeneous energy deposition in the depth direction because the LET profile varies as shown in *Figure 2.* Given the results, it therefore appears that the deterioration of mechanical properties can be interpreted with only the 'average' absorbed dose. The slight increase in tensile strength at higher dose indicates domination by crosslinking in PE, an effect common to all irradiation conditions.

Irradiation effects on mechanical property of PTFE. Figure 3 shows the changes in elongation and tensile strength at break for PTFE as a function of absorbed dose. The results for PTFE are similar to those for PE, namely, the elongation and tensile strength at break decreased with dose, but without a dependence on the type of irradiation, even though the LET varies by two orders of magnitude. We have previously observed that the changes in tensile properties of PTFE are similar for 2 MeV electron, H^+ 45 MeV[11] (10.2 $MeV\,cm^2\,g^{-1}$), and H^+ 10 MeV[1] (36.5 $MeV\,cm^2\,g^{-1}$). Our current studies show that the degradation is the same for LETs of 879.5 $MeV\,cm^2\,g^{-1}$ (C^{5+} 220 MeV ions) and 4515 $MeV\,cm^2\,g^{-1}$ (O^{5+} 100 MeV ions, on average) regardless of the inhomogeneity in LET in the depth direction (He^{2+} 20 MeV, O^{5+} 100 MeV ions).

LET effect on mechanical properties. The results of this study show that the deterioration behaviour of tensile properties for PE and PTFE is essentially independent of the ion used for irradiation. One possible explanation is that an LET effect may exist but the mechanical properties are insensitive to this effect. On the other hand, it is also possible that 'a threshold LET'[8], the LET below which irradiation effect is identical and above which irradiation

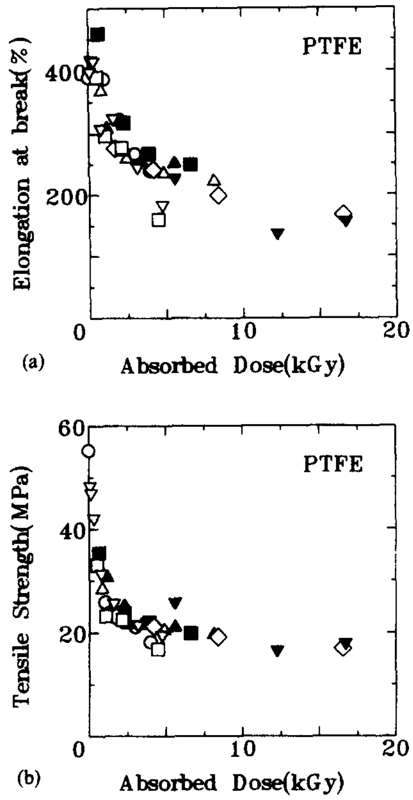


Figure 3 (a) Elongation at break. (b) Tensile strength of PTFE irradiated with: ■, He^{2+} 50 MeV; □, He^{2+} 20 MeV; ▽, C^{5+} 220 MeV; ▼, O^{5+} 100 MeV, respectively. ○, 2 MeV electron under vacuum; △, H^+ 10 MeV; ▲, H^+ 45 MeV; ◇, D^+ 10 MeV

effect shows LET dependence, exists and is much larger than that of O^{5+} 100 MeV ions. However, this latter idea seems to be unreasonable, because the threshold LET is of the order of a few eV $Å^{-1}$ for PMMA and CTA[8] in terms of molecular weight or colour change. The threshold LET itself should be similar for CTA, PMMA and PE, because they contain the same nuclei, and they are solid state aliphatic polymers. The authors therefore favour the former idea. The deterioration of material properties seems to be almost independent of LET and depend mainly on the average dose for the whole specimen or the energy deposition at the surface, for PE and PTFE. We found that PE irradiated by H^+ 10 MeV ions showed almost the same deterioration behaviour as PE irradiated by 2 MeV electrons, whereas H^+ 10 MeV caused gelation more effectively than 2 MeV electrons[1]. The crosslink probability is expected to increase in high LET radiation. Since mechanical properties are not simply related to molecular weight, they may be somewhat insensitive to an LET effect. On the other hand, the deterioration state at the surface sometimes determines the material properties. For example, it is reported that the oxidation at the surface determines the elongation of polymer materials[12]. However, at this moment, it is impossible to tell which of the average dose or the energy deposition at the surface determines the material properties, because the energy deposition at the surface is not so different from the average for the whole specimen.

Conclusion

High energy heavier ion irradiation effects on PE and PTFE were studied by monitoring changes in elongation at break. Similar degradation behaviour was found for all types of irradiation, implying that the degradation of mechanical properties is less sensitive to the LET and depends mainly on absorbed dose.

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