JOURNAL OF MATERIALS SCIENCE 24 (1989) 1570–1574

Electron-beam irradiation effects on mechanical properties of PEEK/CF composite

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Carbon fibre-reinforced composite (PEEK/CF) using polyarylether-ether-ketone (PEEK) as a matrix material was prepared and electron-beam irradiation effects on the mechanical properties at low and high temperatures were studied. The flexural strength and modulus of the unirradiated PEEK/CF were almost the same as those of carbon fibre-reinforced composites with epoxide resin. The mechanical properties at room temperature were little affected by irradiation up to 180 MGy, but in the test at 77 K the strength of the specimens irradiated over 100 MGy were slightly decreased. The mechanical properties of the unirradiated specimen decreased with increasing testing temperature, but the high-temperature properties were improved by irradiation, i.e. the strength measured at 413 K for the specimen irradiated with 120 MGy almost reached the value for the unirradiated specimen measured at room temperature. It was apparent from the viscoelastic measurement that the improvement of mechanical properties at high temperature resulted from the high-temperature shift of the glass transition of the matrix PEEK caused by radiation-induced cross-linking.

1. Introduction

Continuous carbon fibre-reinforced composites with high performance thermoplastics as matrix materials, such as polyphenylenesulphide (PPS) and polyarylether-ether-ketone (PEEK), are now available. It has been reported that these composites show excellent inter-laminar toughness and resistance to delamination in comparison with composites having thermosetting matrix resin [1–4].

In the studies of radiation effects on a number of aromatic polymers having various chemical structures, among the thermoplastics studied PEEK showed the excellent radiation resistance under various radiation conditions [5–7]. It is presumed that a high-performance composite with high stability for radiation is realized by combining carbon fibre with PEEK.

Actual radiation fields are very varied: for instance, the materials used around a fast neutron breeder are irradiated with a high dose (over 100 MGy) at high temperature; the insulating materials used in the superconducting magnet of a fusion reactor are irradiated with over 50 MGy at low temperature; and in space the materials are irradiated by a large number of electrons and other particles such as protons under thermal cycles of low to high temperatures. For the application of composite materials in such environments, knowledge of the radiation effects on mechanical and other properties under various conditions is needed. As a first step of a series of studies, high dose rate electron-beam irradiation effects on mechanical properties at low and high temperatures and the effects of thermal experience after irradiation were studied.

2. Experimental procedure

2.1. Materials

A prepreg was prepared by impregnating PEEK directly into Torayca 6142 plain fabrics of carbon fibre in the molten state. The 18 plies of laminate were obtained by compression moulding in a press at 673 K. The fibre volume fraction was 58% and the thickness was about 2 mm. The specimen was cooled slowly down to 323 K after moulding, then the degree of crystallinity of the matrix PEEK reached maximum crystallinity (25 to 30%). The specimens for measurements of mechanical properties were cut to measurements of 6.5 mm wide and 75 mm long. The sample for measurement of viscoelastic properties was specially prepared by lamination of four plies of prepregs, of dimensions 0.45 mm thick, 10 mm wide and 100 mm long.

2.2. Irradiation

Irradiation was carried out in air using a 2 MeV electron beam from a Dynamitron IEA-300-25-2 accelerator installed at JAERI Takasaki. Each specimen was wrapped with aluminium foil, 20 μm thick, and attached to a water-cooled stainless steel plate using a conducting adhesive, to prevent temperature rise of the specimen during irradiation. The dose rate measured using a cellose triacetate (CTA) film dosimeter was 5 kGy sec^{-1}.

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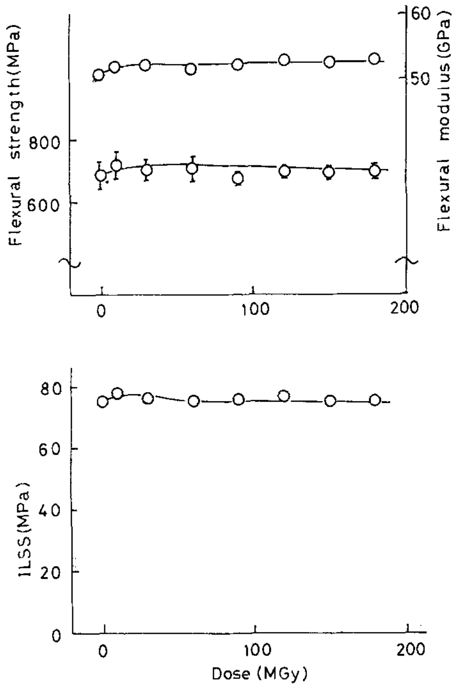

Figure 1 Dose dependence of flexural strength, modulus and ILSS of PEEK/CF in the tests at room temperature.

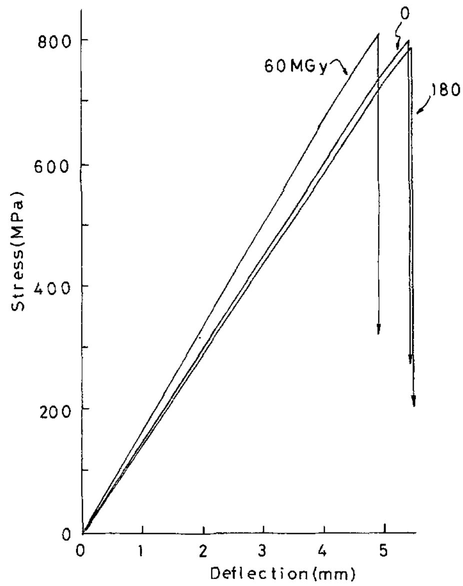

Figure 2 Typical stress–deflection curves PEEK/CF irradiated with various doses.

2.3. Evaluation of radiation effects

Radiation effects were evaluated from the changes in the flexural strength and flexural modulus and interlaminar shear strength (ILSS). The span length for the bending tests was 35 mm (span/width ratio = 17.5) and the cross-head speed was $2\,\mathrm{mm\,min^{-1}}$. The testing temperatures were 77 K, room temperature and high temperatures (373, 413, and 453 K). The test at 77 K was carried out by directly immersing the specimens into liquid nitrogen, and the tests at high temperature were carried out in an air-circulating thermostat oven. ILSS measurement was made on the specimens of dimensions 15 mm × 15 mm at room temperature with a cross-head speed of $2\,\mathrm{mm\,min^{-1}}$.

Viscoelastic measurements were performed using a torsion pedulum-type viscoelastometer (RHESCA RD-1100 AD) with a frequency range of 0.5 to 1 Hz in the temperature range 120 to 590 K.

3. Results and discussion

3.1. Radiation effects on the properties at room temperature

The flexural strength, flexural modulus and ILSS which were measured at room temperature are shown as a function of dose in Fig. 1. The strength, modulus and ILSS for the unirradiated specimen are 681 MPa,

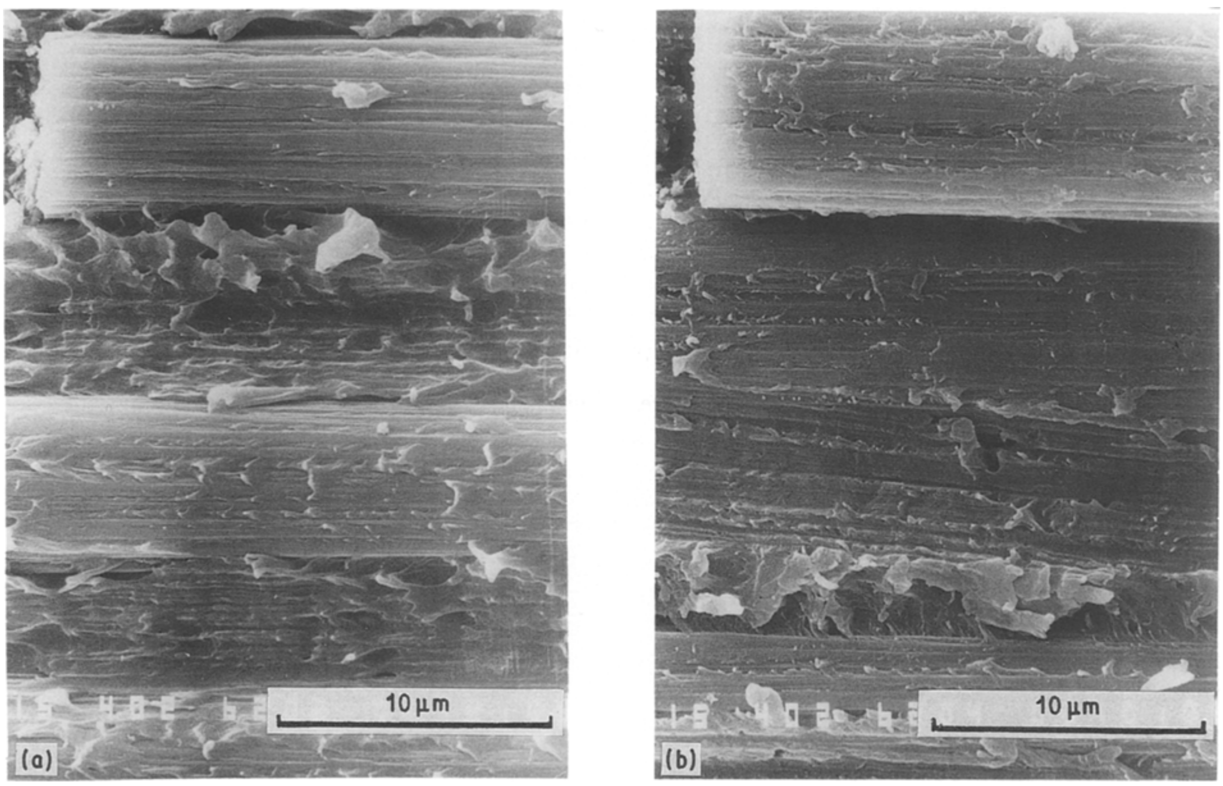

Figure 3 Fractography of PEEK/CF irradiated with (a) 30 MGy and (b) 120 MGy.

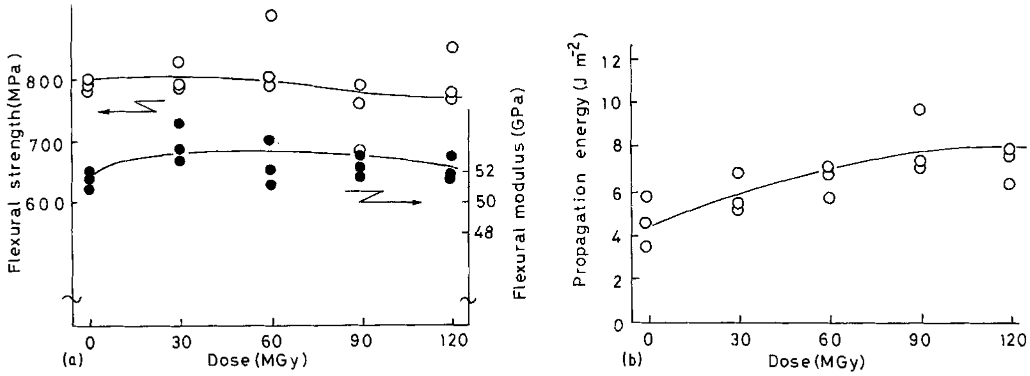

Figure 4 Dose dependence of (a) flexural properties and (b) propagation energy of PEEK/CF in the tests at 77 K.

51 GPa and 75 MPa, respectively. These values are comparable to the values for CFRP using thermosetting epoxide resin as the matrix. The strength, modulus and ILSS increase slightly with dose in the initial stage, and then remain constant up to 180 MGy.

Typical stress–deflection curves of the specimens irradiated with various doses are shown in Fig. 2. In all cases, the stress increases linearly upon deflection to a maximum and then decreases sharply, indicating that this composite is fractured by fibre failure mode even after irradiation with 180 MGy. Fig. 3 shows the fractography of the specimens irradiated with 30 and 180 MGy. The matrix PEEK irradiated with 180 MGy seems to become brittle but fractography demonstrates that the composite is fractured by fibre failure. Observation of Figs 1 to 3 reveals that the mechanical properties at room temperature of PEEK/CF are little affected by irradiation up to 180 MGy.

3.2. Radiation effects on low-temperature properties

The flexural strength and modulus measured at 77 K are shown as a function of dose in Fig. 4a. On cooling to 77 K, the flexural strength of the unirradiated specimen increases by 1.14 times. Although it was reported that PEEK became brittle below 77 K [8], PEEK/CF retains excellent performance even at 77 K. This shows that PEEK has sufficient potential for use as a matrix material at low temperatures. In irradiated specimens, the data points show some scattering and the mechanical properties seem to decrease slightly in the high-dose region. In Fig. 4b, the fracture propagation energy calculated from the area under the stress–deflection curves after yielding, is shown. The propagation energy increases with dose, showing that interlaminar toughness at low temperature decreases somewhat with dose. It can be concluded that the mechanical properties at low temperature decrease slightly in the high-dose region.

3.3. Radiation effects on high-temperature properties

Fig. 5 shows the dose dependences of the flexural strength and modulus measured at various temperatures. The strength and modulus of the unirradiated specimen decrease with increasing testing temperature, for instance, the strength at 413 K is about 70% of that at room temperature. On the contrary, in irradiated specimens, the mechanical properties at high temperature are improved with increasing pre-irradiation dose; for example, the flexural strength measured at 413 K of the specimen irradiated with 120 MGy approaches that of the unirradiated specimen measured at room temperature.

Typical load–deflection curves obtained in the bending tests at high temperature are shown in Fig. 6. In the test below 373 K, the load of the unirradiated specimen decreases sharply after yielding, but above 413 K the load decreases stepwise after yielding. This might be brought about by interlaminar shearing resulting from increasing mobility of matrix PEEK. In the specimens irradiated with over 30 MGy, the load decreases sharply after yielding, even at 413 K.

Fig. 7 shows temperature dependence of the mechanical loss factor (logarithmic decrement) and dynamic shear modulus of PEEK/CF irradiated with various doses. Two mechanical relaxation processes are

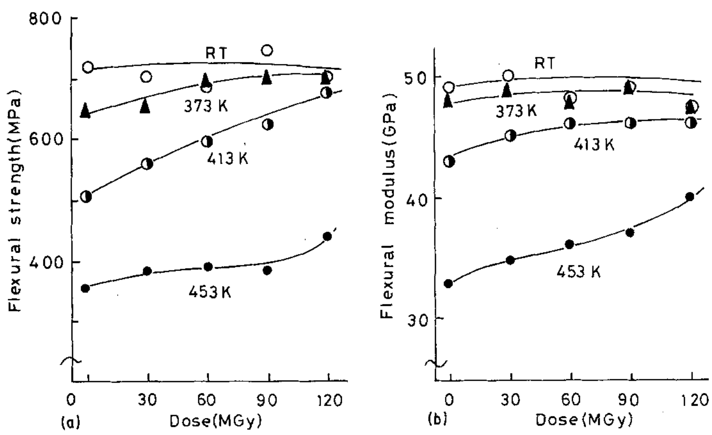

Figure 5 Dose dependence of (a) flexural strength and (b) modulus of PEEK/CF measured at various high temperatures.

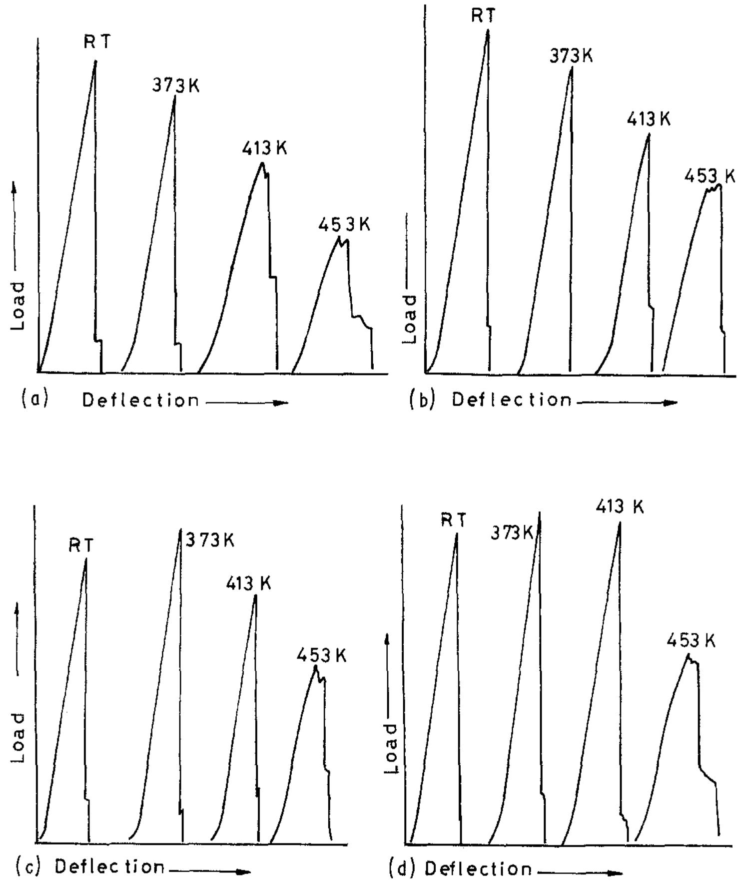

Figure 6 Typical load–deflection curves of PEEK/CF in the tests at various high temperatures, and at (a) original, (b) 30 MGy, (c) 60 MGy, (d) 120 MGy.

visible; each relaxation is named γ and β relaxation from the low to high temperature. The γ relaxation of polymers having rigid-chain configuration, such as PEEK and polysulphones, is attributed to local motion of the main chain itself in the glassy state [9–14]. In the case of PEEK, the γ relaxation is responsible for local motions of diphenylether, diphenylketone and their combined moieties [13, 14]. The peak temperature and the profiles of the γ relaxation are changed by irradiation. This was deduced from viscoelastic studies on non-crystalline and semi-crystalline PEEK as a result of partial damage in diphenylether and diphenylketone moieties [13, 14].

The β relaxation is attributable to a three-dimensional motion of main chains in the process of glass transition, because the shear modulus decreases sharply at the same time. By irradiation the β relaxation peak shifts to higher temperature with dose, showing that the glass transition temperature increases with increasing dose. The high-temperature shift of glass transition indicates the formation of bulky structure and/or cross-linkage by irradiation. It was shown from the same studies on non-crystalline PEEK that the higher temperature shift of the glass transition is brought about by formation of cross-linking [13].

The β-peak temperature measured with low frequency is known to correspond well to the glass transition temperature obtained in steady state. The result in Fig. 7 shows that the glass transition

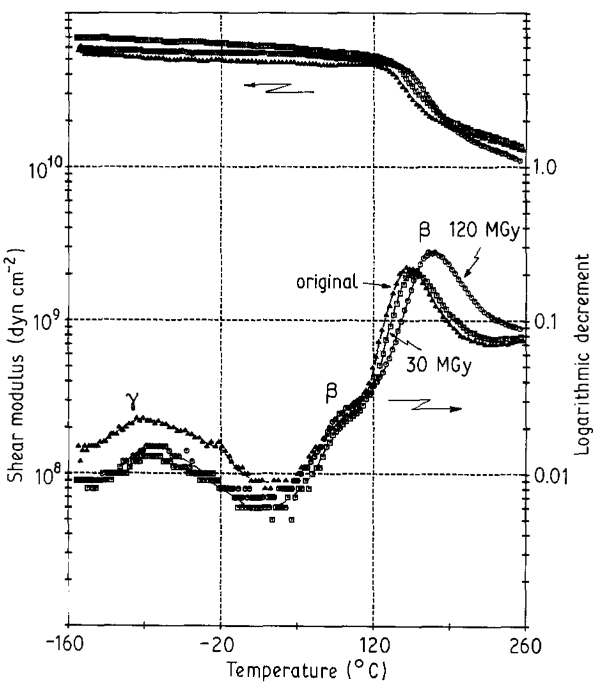

Figure 7 Viscoelastic spectra of PEEK/CF irradiated with various doses.

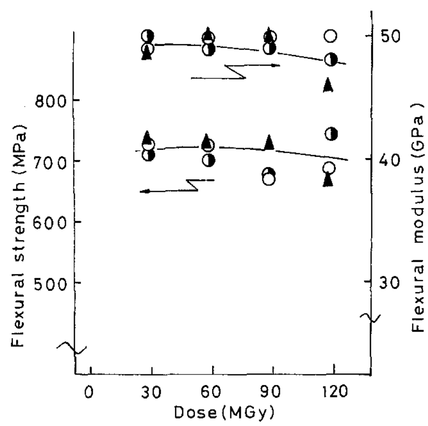

Figure 8 Dose dependence of flexural properties of PEEK/CF subjected by thermal treatment at various temperatures after irradiation; (○) 353 K, (▲) 393 K, (◑) 423 K.

temperature increases to 429 from 427 K by irradiation with 30 MGy and to 450 K by irradiation with 120 MGy. It can be concluded that the improvement of mechanical properties at high temperature by irradiation is brought about by high-temperature shift of the glass transition of the matrix PEEK and formation of cross-linking in PEEK.

3.4. Effects of thermal treatment after irradiation

It was reported that the flexural strength of a CFRP using epoxied resin as the matrix, decreased strongly as a result of thermal treatment after irradiation [15]. This strong deterioration was explained by further increase of radiation damage in the matrix by thermal experience.

Fig. 8 shows the dose dependence of the flexural strength and modulus for the specimens subjected by thermal treatment at various temperatures after irradiation up to 120 MGy. The strength and modulus of the specimens irradiated above 90 MGy are slightly decreased by the thermal treatment, but the load–deflection curves shown in Fig. 9 show that the fracture mode is not affected by the thermal treatment after irradiation. It can be seen that thermal resistance of the matrix PEEK is little affected by irradiation.

4. Conclusion

The high dose rate electron-beam irradiation effects on PEEK/CF are summarized as follows.

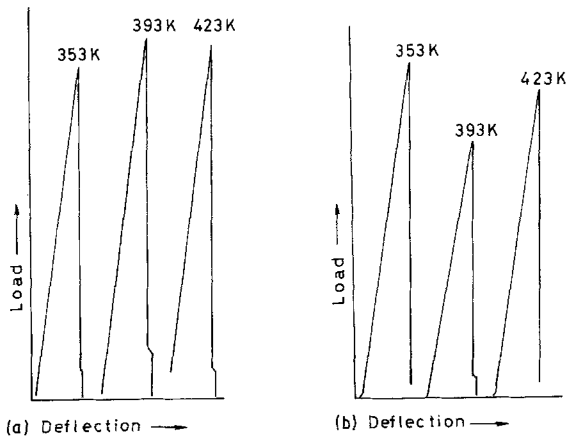

Figure 9 Typical load–deflection curves of PEEK-CF subjected to thermal treatment at various temperatures after irradiation at (a) 30 MGy, and (b) 120 MGy.

1. The mechanical properties at room temperature are little affected by irradiation up to 180 MGy.
2. At 77 K, the contribution of delamination to fracture is slightly increased by irradiation, but PEEK/CF shows excellent mechanical properties at low temperature after irradiation up to 120 MGy.
3. The mechanical properties at high temperature are improved by irradiation; this is caused by increasing the glass transition temperature of the matrix PEEK and the formation of cross-linking in PEEK.
4. Mechanical properties are little affected by thermal treatment after irradiation, indicating that the matrix PEEK retains excellent thermoresistance after irradiation up to 120 MGy.

Acknowledgements

The authors thank Mr Hirosi Itoh for SEM observation and Dr Sigenori Egusa for bending tests at low temperature.

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Received 14 March and accepted 27 July 1988