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Ion irradiation effects on thermal and mechanical properties of poly(ether–ether–ketone) (PEEK)

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Abstract

The change in thermal properties induced by irradiation of 10 MeV H^+, 20 MeV He^{2+} and 2 MeV electron were studied for non-crystalline and crystalline poly(ether–ether–ketone) (PEEK), PEEK-a and PEEK-c, by differential scanning calorimetry (DSC). It was revealed from the analysis of thermal parameter changes that crosslinking proceeds by irradiation in all cases studied. The comparison of effects between ion and electron irradiations led to a conclusion that probability of crosslinking in the ion irradiation is extremely large compared with that in the electron irradiation. It was clarified from isothermal crystallization that ion gives more severe damage to crystallite than electron. The tensile properties for PEEK-a were varied in accord with difference in thermal properties between ion and electron irradiations, whereas for PEEK-c the difference in those between ion and electron irradiations was scarcely observed.

Keywords: H^+beam; He^{2+}beam; Electron irradiation

1. Introduction

Poly(ether–ether–ketone) (PEEK) has been paid an attention as not only a high performance heat resistant engineering plastic but also a matrix resin for an advanced carbon fiber reinforced thermoplastic (CFRTP) [1–4]. Radiation effects on PEEK induced by electron and gamma rays have been studied and reported that it has excellent radiation resistance over 50 MGy in the non-oxidative irradiation (high dose rate of electron in air and gamma rays in vacuo) and that the main mechanism for property change is crosslinking [5–11]. Because of its high heat and radiation resistances, PEEK is a good candidate for use in radiation fields, especially, PEEK-CFRTP is expected as a material used in space environment. For the application of PEEK in the space environment, knowledge about radiation resistance for cosmic rays like high-energy proton and heavy ions is required.

It is known that irradiation effects on organic materials are changed by energy deposition rate per track length ($-dE/dx$) of radiation sources [12–25]. The $-dE/dx$ is called as a linear energy transfer (LET) and the LET of energetic charged particles is extensively large compared with that of MeV electrons and Co-60 γ rays. There are many reports on LET effects on G-values (the number of chemical events per 100 eV energy absorption) of crosslinking (G_x) and/or chain scission (G_s) of polymers [16–25]. It has been reported, in general, that G_x increases and G_s decreases in irradiation of ions with high LET. This phenomenon was interpreted in terms of high-density excitation and high probability of recombination of active species.

We have studied changes in mechanical properties induced by high-energy ions such as H^+(10–45 MeV), He^{2+} (20–50 MeV), O^{5+} (100 MeV), and C^{5+} (220 MeV) for several polymers [26–31]. In comparison with the results of the electron irradiation, the following tendency has been observed; characteristic effect of ion irradiation is scarcely observed in aliphatic polymers but it is observed in aromatic polymers. Hill et al. [32], however, reported that little difference was found on the deterioration of the mechanical properties of aromatic polyimide film between irradiations of 3 MeV proton and γ-rays/electron. This work was planned to accumulate further knowledge about ion irradiation effects on aromatic polymer.

To clarify ion irradiation effects on polymer crystals is another aim of the present study. It has been reported from the study of radiation effects on polyethylene single crystal mat and polymers having various degree of crystallinity that the chains existing in crystallites are hardly affected by irradiation [33–36]. PEEK turns to non-crystalline state

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Table 1
Stopping power and projectile range of ions calculated by TRIM 95 code

Ions	Polymer	Stopping power (MeV $cm^2 g^{-1}$)	Projectile range (μm)
H^+ 10 MeV	PEEK-a[a]	43.75	1010
	PEEK-c[b]	43.75	978
He^{2+} 20 MeV	PEEK-a[a]	307.0	298
	PEEK-c[b]	307.0	288

[a] PEEK-a; non-crystalline PEEK.
[b] PEEK-c; crystalline PEEK.

by quenching from molten state and becomes to semi-crystalline state by thermal treatment above the glass transition temperature. For the study of irradiation effects on polymer crystal, it is worthwhile to use crystalline and non-crystalline PEEKs with the same molecular structure.

Further, in this work, the relation between microscopic change and mechanical property was briefly studied.

2. Experimental

2.1. Samples and irradiation

Non-crystalline and crystalline PEEKs were used, termed as PEEK-a and PEEK-c, respectively. These were received as film form with 100 μm thickness and their densities are 1.256 and 1.300 g cm^{-2}.

Ion irradiation was performed in an ion beam irradiation facility at Takasaki Radiation Chemistry Research Establishment, JAERI. In this facility, specimens can be irradiated on wide area of 100 mm × 100 mm by scanning spot ion beam (about 10 mm diameter). Ions used were 10 MeV H^+ and 20 MeV He^{2+}. The details of irradiation method were described in the previous article [31]. The current of the spot beam was about 300 nA for H^+ and about 100 nA for He^{2+} irradiation.

The stopping power and projectile range of materials for each ion were calculated by TRIM 95 code and are listed in Table 1. The irradiation was performed on the stack of films of PEEK-a and PEEK-c; the first layer is PEEK-a and second layer is PEEK-c. When ions pass through the first layer, ions lose energy, and especially energy loss is large in the case of 20 MeV He^{2+}. Table 2 shows the energy losses upon passing through the PEEK-a film and the inlet energy to the second film (PEEK-c). Absorbed dose (D) is calculated by following relation:

$$D(\mathrm{kGy}) = S(\mathrm{MeV\ cm^2 g^{-1}}) \times Q(\mu\mathrm{C\ cm^{-2}})/Z_{\mathrm{inc}}.$$

where S is mass stopping power of material, Z_{inc} is charge number of incident ion and Q is the fluence. The absorbed dose of PEEK-a was calculated based on the incident energy and that of PEEK-c was calculated based on the inlet energy after ions passed through PEEK-a film. The evaluated dose is listed in Table 3.

Table 2
Energy loss (MeV) of ions after passed through the first layer (PEEK-a) calculated by TRIM 95 code. (*Irradiation*: The PEEK-a film with 100 μm thickness was stacked on the PEEK-c film with the same thickness and was irradiated by ion beam)

Ions	Energy loss (MeV)	Energy at the surface of the second layer (MeV)
H^+ 10 MeV	0.60	9.40
He^{2+} 20 MeV	4.32	15.68

Electron irradiation was carried out by using 2 MeV scanning electrons from an accelerator in a vacuum chamber. The absorbed dose for electron was measured by using a cellulose tri-acetate (CTA) film dosimeter and corrected by the same method described in the previous article [31].

2.2. Measurement

Thermal properties were measured by using a differential scanning calorimeter (DSC-7, Perkin–Elmer). Measurements were carried out in N_2 atmosphere at heating and cooling rate of 20°C min^{-1}. The first heating run to 350°C at which the material is completely melted, cooling run from 350°C and the second heating run were sequentially performed.

Isothermal crystallization was performed in DSC and its procedure is as follows:

1. the sample was heated up to 350°C at the heating rate of 300°C min^{-1} and held at this temperature for 20 min to complete radical decay and melting;
2. the sample was then cooled down to a crystallization temperate at the rate of 300°C min^{-1} and then crystallized isothermally till the heat flow was unchanged.

Tensile tests were performed on JIS No 4 type dumbbell under the condition of 200 mm min^{-1} cross head speed at room temperature. Average and standard deviation of 6 to 7 specimens represent as the data.

3. Results

3.1. DSC thermogram

Fig. 1 shows the first heating, cooling and second heating curves for the unirradiated PEEK-a. An abrupt specific heat

Table 3
Dose evaluation

Ions	Energy at surface (MeV)	Stopping Power (MeV cm^2 g^{-1})	Total charge (μC)	Area (cm^2)	Fluence (μC/cm^2)	Dose (MGy)
PEEK-a						
H^+ 10 MeV	10.0	43.8	14 420	100	144.20	6.3
He^{2+}20 MeV	20.0	307.0	3950	84.75	46.61	7.2
He^{2+}20 MeV	20.0	307.0	8000	84.75	94.40	14.5
PEEK-c						
H^+10 MeV	9.40	46.5	14 420	100	144.20	6.7
He^{2+} 20 MeV	15.68	382.4	3950	84.75	46.61	8.9
He^{2+} 20 MeV	15.68	382.4	8000	84.75	94.40	18.1

change, exothermic and endothermic peaks are observed around 150, 175 and 330°C in the first heating curve. These heat flow changes are attributed to glass transition, crystallization and melting of crystallites, respectively, by referring the results of dynamic viscoelastic measurements [8,9]. The exothermic peak in the cooling run arises from recrystallization from the molten state. As the specimen turned to semi-crystalline state during the cooling run, the exothermic peak owing to crystallization is not observed and the specific heat change owing to glass transition becomes unclear in the second heating curve.

Fig. 2 shows the DSC thermogram for PEEK-a irradiated by He^{2+} (20 MeV) with 7.2 MGy. The profiles of the heating and cooling curves are similar to those for the unirradiated specimen, but the glass transition and crystallization peak shift to higher temperature and the melting peak shifts to lower temperature.

Fig. 3 shows the first heating curves of PEEK-a irradiated by He^{2+} (20 MeV) to 7.2 MGy and 14.5 MGy and by 2 MeV electron to 18 MGy. The glass transition of the specimen irradiated by He^{2+} (20 MeV) to 14.5 MGy shifts extremely to high temperature (214.8°C). Further, the crystallization and melting peaks are diminished in the first heating curve, even though the both peaks are observed in the specimen irradiated by the electron to 18 MGy. The recrystallization no longer occurred in the cooling run.

Fig. 4 shows the first heating curves of PEEK-c unirradiated and irradiated by the electron to 8.9 MGy, He^{2+} (20 MeV) to 8.9 and 18.9 MGy. Since PEEK-c is in semi-crystalline state, the exothermic peak responsible for crystallization is not observed. In contrast to the case of PEEK-a, the melting peak is observed for PEEK-c irradiated by He^{2+} (20 MeV) to 18.9 MGy.

3.2. Details of change in thermal properties

The thermal parameters for the unirradiated PEEK-a and PEEK-c are shown in Table 4. In the first heating run, PEEK-a has lower glass transition temperature (T_g) than PEEK-c (154.7°C). After recrystallization, T_g of PEEK-a rises to 149.4°C, which is equal to the one of PEEK-c in the second heating run. In the second heating run, there is little difference between PEEK-a and PEEK-c in recrystallization temperature (T_{rc}) and heat of crystallization (ΔH_{rc}), melting temperature (T_m) and heat of melting (ΔH_m).

The thermal parameters are shown as a function of dose in

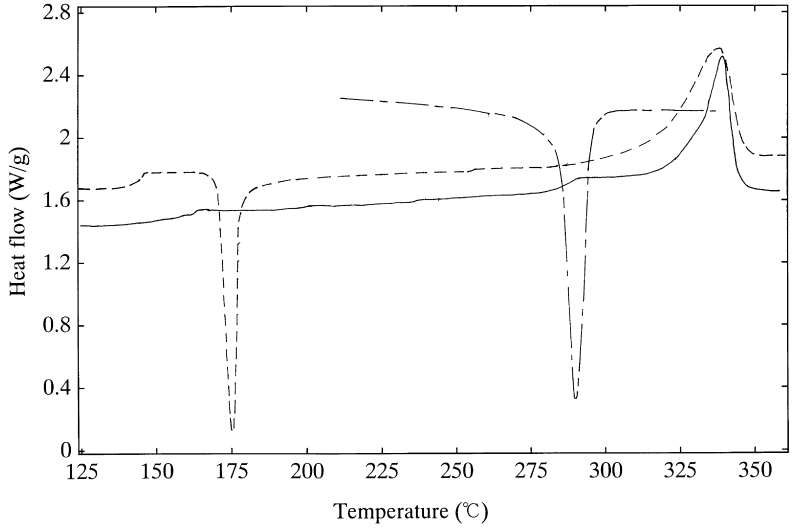

Fig. 1. DSC thermogram for unirradiated PEEK-a, ––; first heating run, -----; cooling run, and —; second heating run.

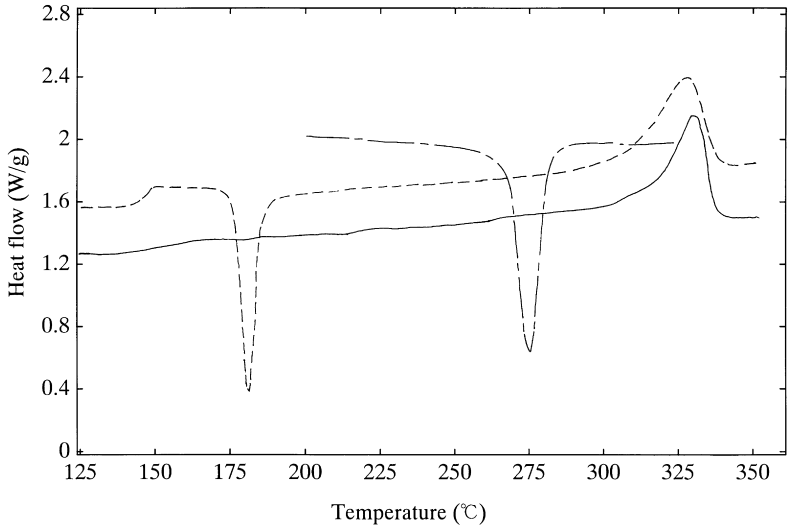

Fig. 2. DSC thermogram for PEEK-a irradiated by He^{2+} (20 MeV) with 7.2 MGy, ––; first heating run, -–––; cooling run, and —; second heating run.

Figs. 5–8. The data was plotted as the form of difference from the value of the unirradiated specimen. Fig. 5 shows the dose dependence of glass transition temperature change (ΔT_g). The ΔT_g increases with dose in all cases studied. The ΔT_g for the specimens irradiated by ions deviate to higher value from the one irradiated by electron. Especially, the deviation in the first heating run for PEEK-c is considerably large compared with that for PEEK-a.

Fig. 6 shows the changes in crystallization temperature (ΔT_c) and heat of crystallization (ΔH_c change) against dose. The T_c shifts to high temperature and ΔH_c decreases with dose. The changes in ΔT_c and ΔH_c induced by ion irradiation deviate from those in the electron irradiation.

Fig. 7 shows the changes in recrystallization temperature (ΔT_{rc}) and heat of recrystallization (ΔH_{rc} change) with dose for PEEK-a and PEEK-c. The two parameters decrease with dose in all cases. The ΔH_{rc} change with dose for PEEK-a in the electron irradiation is larger than that for PEEK-c. The deviation of ΔH_{rc} change by ion irradiation from that by electron irradiations for PEEK-c is fairly large compared with that for PEEK-a.

The changes in melting temperature (ΔT_m) and the heat of melting (ΔH_m change) are shown as a function of dose for PEEK-a and PEEK-c in Fig. 8. The two parameters decrease with dose in all cases. The deviation of ΔT_m for PEEK-a irradiated by ion from that in electron irradiation is not so much, but the deviation for PEEK-c is pretty large. In the first heating run, the decrease in ΔH_m with dose for PEEK-c

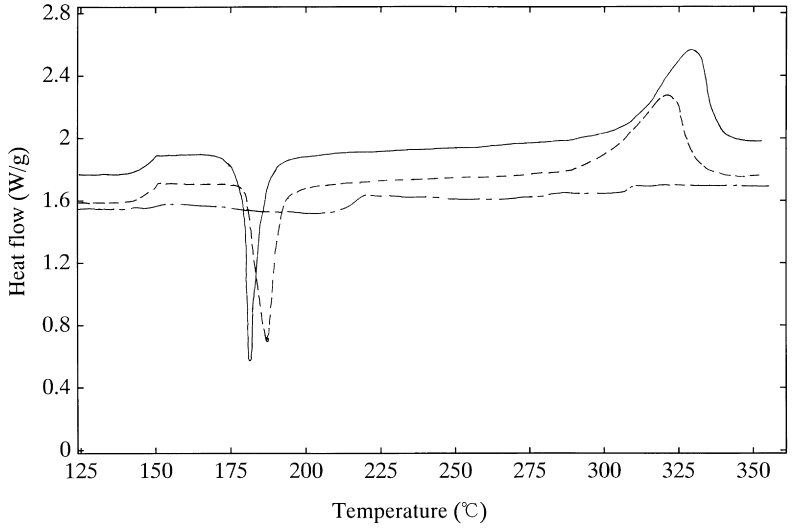

Fig. 3. DSC thermogram for PEEK-a irradiated, ––; by He^{2+} (20 MeV) with 7.2 MGy, -–––; by electron with 18 MGy, and —; by He^{2+} (20 MeV) with 14.5 MGy.

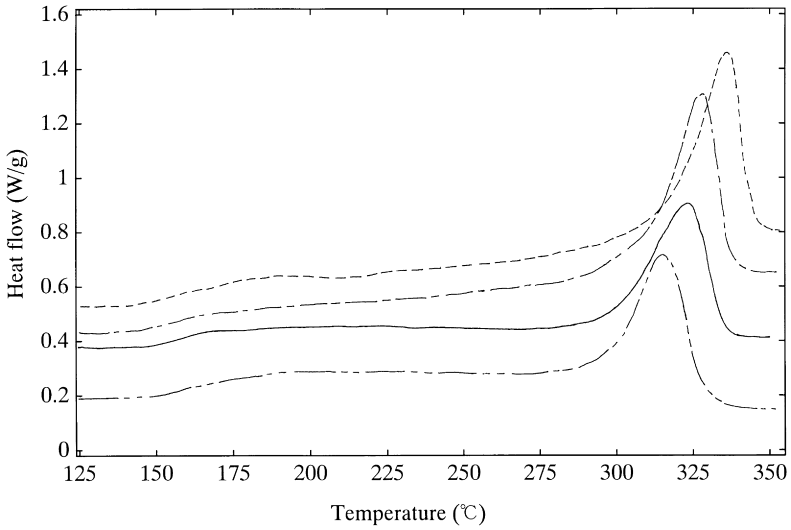

Fig. 4. DSC thermogram for PEEK-c, – – –; unirradiated, - - - -; electron with 8.9 MGy, —; He^{2+} (20 MeV) with 8.9 MGy and –··–··—; by He^{2+} (20 MeV) with 18.1 MGy.

is smaller than that for PEEK-a, and this becomes larger than the first run for the both polymers in the second heating run.

3.3. Isothermal crystallization

Fig. 9 shows a typical isothermal crystallization curves at 310 and 320°C for the unirradiated PEEK-a. The endothermic heat flow is due to crystallization. The time giving maximum endothermic heat corresponds to that for maximum rate of crystallization (TMC).

Fig. 10(a) shows the TMC vs. isothermal crystallization temperature (T_{iso}) curves and heat of isothermal crystallization ($\Delta H_{c,iso}$) vs. T_{iso} curves for PEEK-a unirradiated and irradiated by electron to 7.3 MGy and He^{2+} (20 MeV) to 7.2 MGy. Fig. 10(b) shows the results for PEEK-c unirradiated and irradiated by electron to 8.9 MGy and He^{2+} (20 MeV) to 8.9 MGy. In the temperature and time range in this study, the unirradiated PEEK-a and PEEK-c give the shortest TMC at 295°C and it increases as T_{iso} increases. The rate of crystallization below 295°C was too fast to determine the TMC by the method in this work.

The $\Delta H_{c,iso}$ vs. T_{iso} curves for the both unirradiated specimens show a peak at 320°C. It can be seen that this temperature is the optimum T_{iso} for crystal growth for the unirradiated PEEK. The TMC and $\Delta H_{c,iso}$ vs. T_{iso} curves shift to low temperature side and the magnitude of $\Delta H_{c,iso}$ peak decreases by irradiation. The degree of shifts for the specimens irradiated by ion is larger than that by electron. It is noteworthy phenomena that the peak height of ion irradiated PEEK-a is as same as the one of electron irradiation, contrary that for PEEK-c irradiated by ion is extensively small compared with the one irradiated by electron.

Table 4
Thermal Parameters of unirradiated PEEK-a and PEEK-c

Runs	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PEEK-a					
1st heating	145.0			337.3	40.1
Cooling		176.0	29.5		
2nd heating	149.4	289.4[a]	45.7[b]	338.4	47.1
PEEK-c					
1st heating	154.7			336.6	39.4
Cooling		290.5	45.9		
2nd heating	149.7			338.4	45.4

[a] T_{rc}.
[b] ΔH_{rc}.

3.4. Changes in tensile properties

Fig. 11 shows changes in the tensile properties by irradiation. The tensile strength and elongation for the both polymers decrease monotonically with dose in the electron irradiation. In the ion irradiation, the two tensile parameters for PEEK-a decrease abruptly above 10 MGy, and on the contrary, the changes in those with dose for PEEK-c can be regarded as there is no difference between electron and ion irradiations.

4. Discussion

4.1. General radiation effects

The T_g of the unirradiated PEEK-a in the second heating run shifts to high temperature and the value becomes equal to the one for the unirradiated PEEK-c (Table 4). This shift of T_g to high temperature arises from restriction of three-dimensional molecular motion by the crystallites newly formed during cooling run.

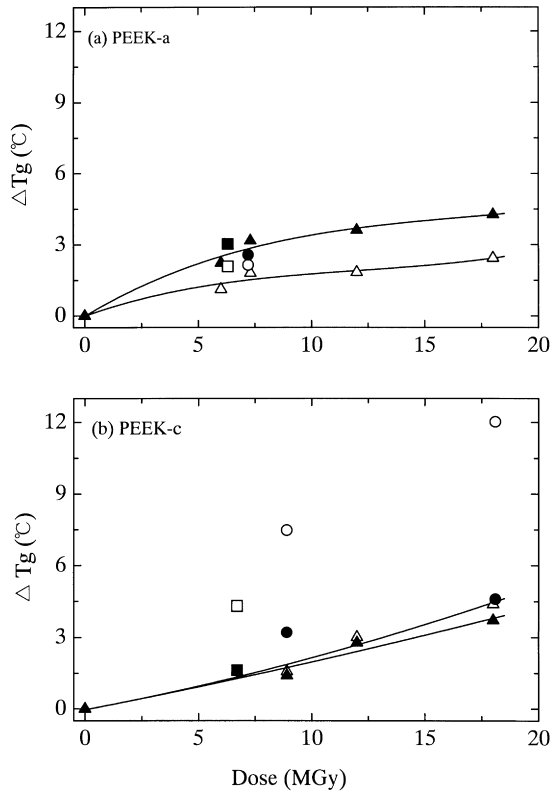

Fig. 5. Dose dependence of ΔT_g for PEEK-a and PEEK-c, △; 2 MeV electron in the first heating, □; H^+ (10 MeV) in the first heating, ○; He^{2+} (20 MeV) in the first heating, ▲; 2 MeV electron in the second heating, ■; H^+ (10 MeV) in the second heating, ●; He^{2+} (20 MeV) in the second heating.

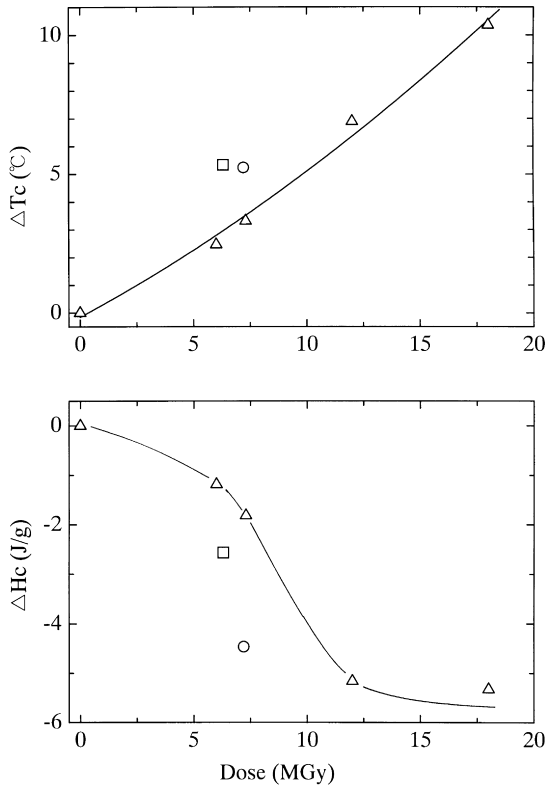

Fig. 6. Dose dependence of ΔT_c and ΔH_c change for PEEK-a, △; 2 MeV electron, □; H^+ (10 MeV), ○; He^{2+} (20 MeV).

Similarly, the T_g shifts to higher temperature by irradiation. According as the rising of T_g, T_c shifts to higher temperature and ΔH_c decreases (Fig. 6), and the T_{rc} and ΔH_{rc} decrease with dose (Fig. 8). The changes in crystallization parameters indicate that molecular rearrangement during crystallization process is restricted by crosslinking formed by irradiation. Consequently, the shift of T_g to high temperature by irradiation is concluded to result from formation of crosslinking.

The manner of change in T_g with dose is different between PEEK-a and PEEK-c (Fig. 5), i.e. the increase in T_g with dose for PEEK-c in the first heating run is larger than that for PEEK-a. The rise of T_g is mainly attributed to restricting molecular motion by crosslink formed in non-crystalline region, and the crystallites in PEEK-c are also likely to enhance this restriction. The increase in T_g for PEEK-a in the second heating run (Fig. 5) is ascribed to both contributions of the newly formed crystallites during cooling run and crosslinking, therefore making the difference little between PEEK-a and PEEK-c.

The decrease in T_m and ΔH_m with dose in both the polymers (Fig. 8) show that crystallinity and degree of crystallinity are reduced by irradiation. However, the underlying phenomena in the first heating run are different between PEEK-a and PEEK-c. That is, the parameter changes for PEEK-a provide information on the nature of the crystallites newly formed during heating run after irradiation, whereas those for PEEK-c are related to the radiation damage of pristine crystallites. The large decrease in ΔH_m for PEEK-a, and the less decrease in ΔH_m for PEEK-c show increase of crosslinking with dose in the non-crystalline region, and less damage of crystallite, respectively.

The melting parameters in the second heating run give the information about radiation effects in the presence or absence of crystallites, because recrystallization condition is the same in both the polymers. The result that decrement of ΔH_m with dose for PEEK-c is less than the one for PEEK-a means less radiation effects in crystalline region also.

4.2. Characteristics of ion irradiation

Each thermal parameter changes essentially in the same manner with the electron and ion doses. Fig. 12(a) and (b) show the comparison between changes in all parameters at a constant dose in the electron and He^{2+} irradiations.

The T_g for PEEK-a shifts to extremely high temperature by the irradiation of He^{2+} (20 MeV) to 14.5 MGy (Fig. 3). Similarly, the T_g in the first heating run for PEEK-c irradiated by ions is extensively high compared with the one irradiated by electron (Fig. 12(b)). These observations indicate that the probability of crosslinking in the ion irradiation

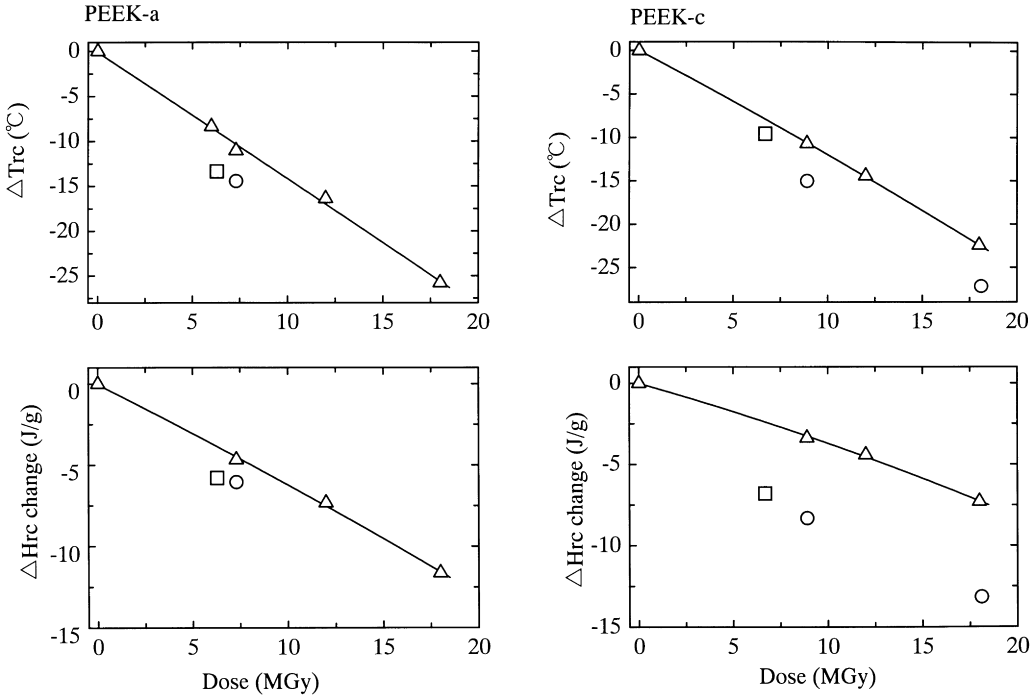

Fig. 7. Dose dependence of ΔT_{rc} and ΔH_{rc} change for PEEK-a ((a), (b)) and PEEK-c ((c), (d)), △; 2 MeV electron, □; H^+ (10 MeV), ○; He^{2+} (20 MeV).

is extremely large compared with the one in the electron irradiation.

The crystallization and melting peaks of PEEK-a are diminished by the irradiation of He^{2+} (20 MeV) with 14.5 MGy (Fig. 3). It has been reported for PEEK that crystallization is suppressed with increase of dose in the electron irradiation, but that crystallization still proceeds after the electron irradiation over 30 MGy [8,9]. Therefore, the present result demonstrates also that the probability of crosslinking in ion irradiation is extensively large. On the

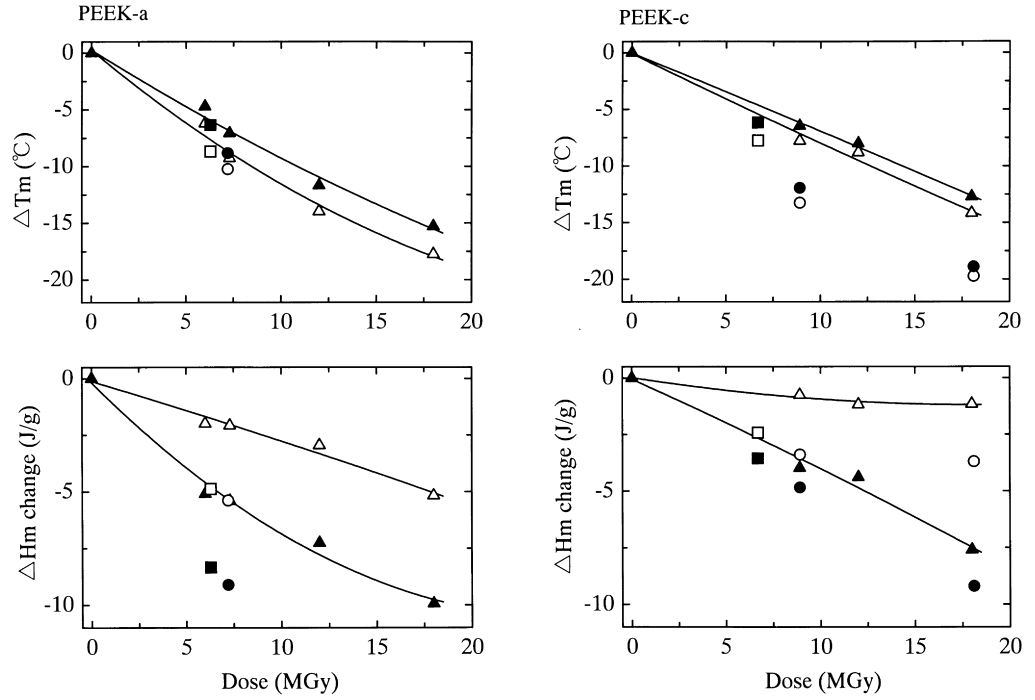

Fig. 8. Dose dependence of ΔT_m and ΔH_m change for PEEK-a and PEEK-c, △; 2 MeV electron in the first heating, □; H^+ (10 MeV) in the first heating,○; He^{2+} (20 MeV) in the first heating. ▲; 2 MeV electron in the second heating, ■; H^+ (10 MeV) in the second heating, ●; He^{2+} (20 MeV) in the second heating.

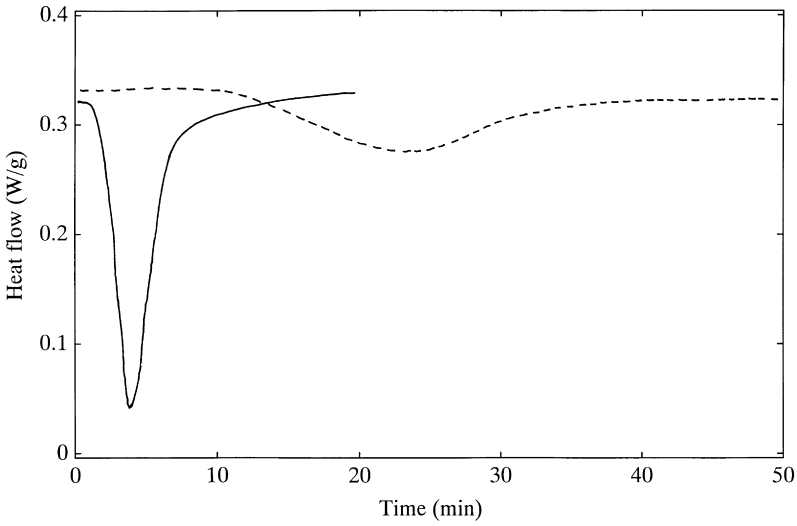

Fig. 9. Isothermal crystallization thermogram for unirradiated PEEK-a, ---; at 310°C, –; at 320°C.

contrary, the melting peak is observed for PEEK-c irradiated by He^{2+} (20 MeV) even after 18.9 MGy (Fig. 4). As the change in melting peak denotes degree of damage of crystallite as discussed before, this fact means that crystallites are less damaged even in ion irradiation. However, the decreases in ΔH_{rc} and ΔH_m in the first heating run for PEEK-c irradiated by ions are fairly large compared with those in the electron irradiation, indicating also that ion causes more damage to crystallite than electron.

The results in the isothermal crystallization shows that the crosslinking formed by irradiation restrict crystallization process and that ion induces larger effects than electron. The $\Delta H_{c,iso}$ for PEEK-c irradiated by He^{2+} (20 MeV) to 8.9 MGy is extensively small compared with that for PEEK-a irradiated by the same ion to 7.2 MGy (Fig. 10). Taking into account the result in the electron irradiation to 8.9 MGy, this fact cannot be interpreted only in terms of higher dose irradiation. Since ion deposits large energy to

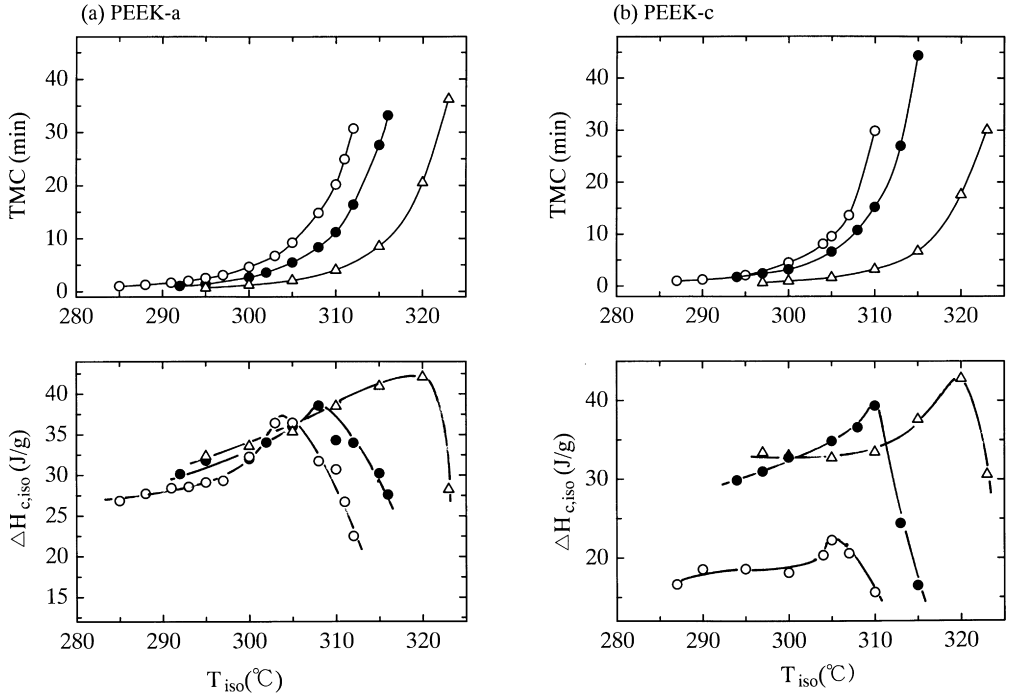

Fig. 10. Results of isothermal crystallization for PEEK-a (a) △; unirradiated, ●; 2 MeV electron with 7.3 MGy, ○; He^{2+} (20 MeV) with 7.2 MGy, and PEEK-c (b), △; unirradiated, ●; 2 MeV electron with 8.9 MGy, ○; He^{2+} (20 MeV) with 8.9 MGy.

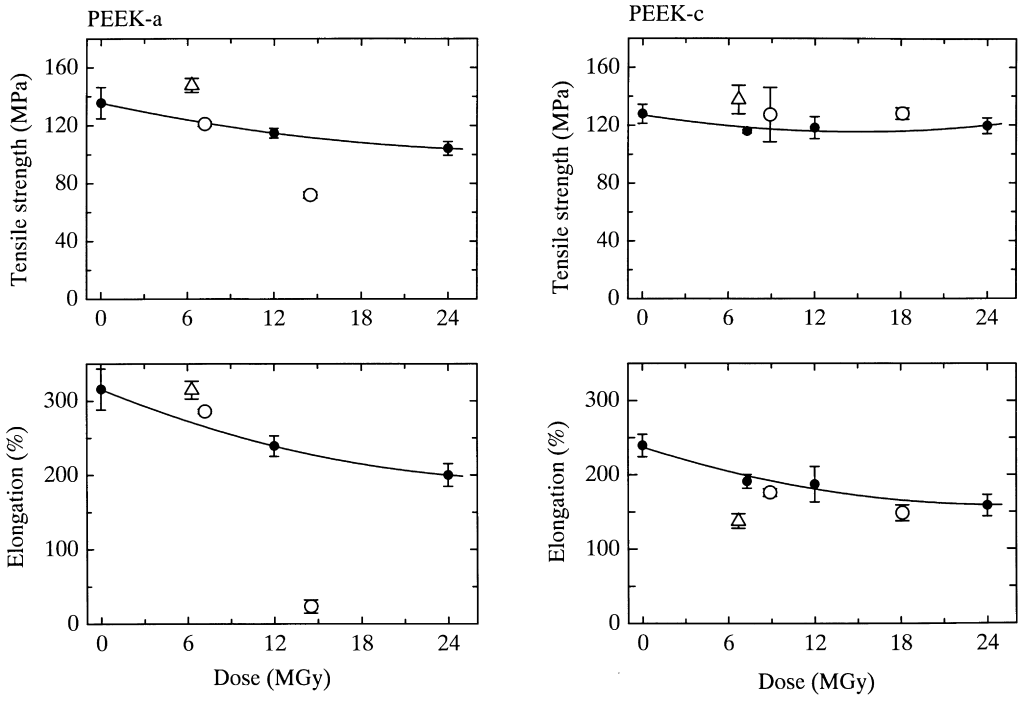

Fig. 11. Dose dependence of tensile properties for PEEK-a and PEEK-c, ●; 2 MeV electron, △; H^+ (10 MeV), ○; He^{2+} (20 MeV).

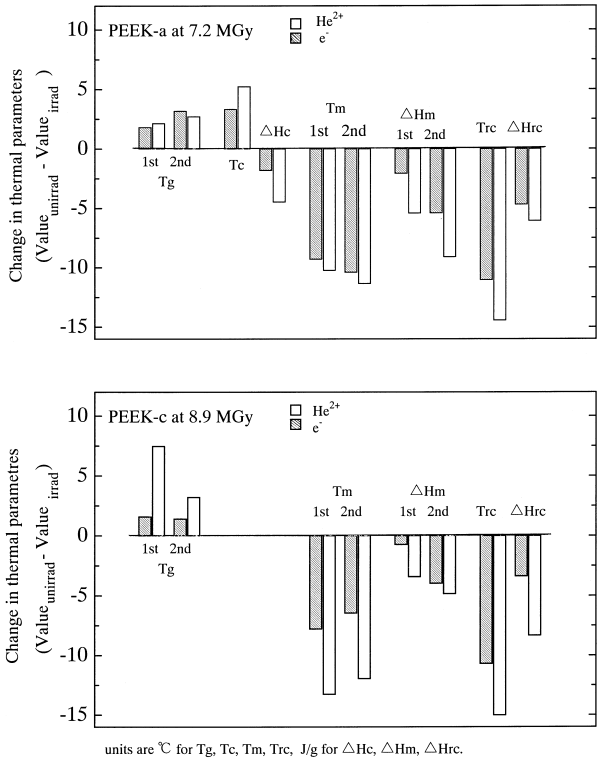

Fig. 12. Comparison of change in thermal parameter between ion (20 MeV He^{2+}) and electron (2 MeV) irradiations.

local area, it could be considered that a different crosslinking structure from the one induced by electron irradiation is created on molecular chains in crystallite. The low $\Delta H_{c,iso}$ in the isothermal crystallization for PEEK-c accords well with the low ΔH_{rc} (Fig. 7).

4.3. Relation to mechanical properties

Since the tensile tests were carried out without any thermal history after irradiation, the change in the thermal properties in the first heating run should be reflected to the change in mechanical properties. The abrupt decrease in the tensile properties of PEEK-a irradiated by He^{2+} (20 MeV) to 14.5 MGy corresponds with the large shift of T_g to high temperature (Fig. 3) and can be interpreted in terms of high-density formation of crosslinking. However, the change in tensile properties of PEEK-c irradiated by He^{2+} (20 MeV) to 18.1 MGy is as same as the one irradiated by electron, despite that ΔT_g for this specimen is fairly large as 12°C. As contribution of crystallites is contained in this large increase in T_g as discussed before, the number of crosslinking points formed in non-crystalline region would not be larger than those in the electron irradiation. It is considered that the increment of the number of crosslinking points are not large enough to alter macroscopic properties from in electron irradiation. Further, as probability of crosslinking for

chains in crystallite is less than in non-crystalline state, the number of crosslinking points is not so much as total in PEEK-c.

5. Summary

The following conclusions are observed based on discussion about the changes in thermal properties by electron and ion irradiations for non-crystalline and crystalline PEEKs.

1. High temperature shift of T_g and T_m and decrease in ΔH_c for PEEK-a are brought about by formation of crosslinking.
2. Similarly, lowering T_{rc} and T_m, and decrease in ΔH_{rc} and ΔH_m are ascribed to formation of crosslinking.
3. It was revealed from comparison of results between ion and electron irradiations that ions give fairly large effect on non-crystalline and crystalline regions compared with electron.
4. The results in isothermal crystallization support the above conclusion and indicate that ion creates a different crosslinking structure on molecular chains in crystallite from the case of electron irradiation.

Mechanical properties for PEEK-a were varied in accord with difference in thermal properties between ion and electron irradiations. In contrast with PEEK-a, in the case of PEEK-c little difference in mechanical properties between ion and electron irradiations was observed, in spite of fairly large deviation of changes in thermal properties between ion and electron irradiations. This would be brought about by less radiation effect in crystallite than in non-crystalline region.

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