Irradiation effects on aromatic polymers: 3. Changes in thermal properties by gamma irradiation

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The effects of gamma irradiation under vacuum on the thermal properties and crystallization behaviour of poly(ether ether ketone) (PEEK-a, amorphous; PEEK-c, crystalline) have been investigated by d.s.c. The glass transition temperature for PEEK-a and PEEK-c increased on gamma irradiation, indicating that crosslinking is the main radiation mechanism for PEEK. The heat and temperature of crystallization for PEEK-a slightly changed on irradiation, indicating that the thermal crystallization process was inhibited by crosslinks because of the restriction in chain mobility. The heat and temperature of recrystallization for PEEK-a and PEEK-c on cooling from the molten state also decreased on irradiation and this is good evidence for crosslink formation in the PEEK structure. The disorder in chemical structure caused by crosslinking resulted in a lowering of the heat and temperature of melting. The effect of crystalline domains on the recrystallization behaviour of PEEK-a and PEEK-c was investigated and the effect of irradiation on the isothermal crystallization of PEEK-a and PEEK-c was also studied.

(Keywords: PEEK; gamma irradiation; thermal properties; isothermal crystallization; d.s.c.)

INTRODUCTION

In recent years, there has been increasing interest in the development and utilization of polymers durable at high temperatures (> 150°C). These polymers usually contain a substantial proportion of aromatic structures, which leads to high mechanical strength and high modulus[1]. The degradation of the mechanical and thermal properties of aromatic polymers by high energy radiation has been investigated, and shows that aromaticity generally promotes higher stability[2–10]. Poly(ether ether ketone) (PEEK) offers excellent thermal stability and superior resistance to common solvents, radiation, fire, abrasion and fatigue[11]. Consequently, PEEK is a good candidate for use in areas such as advanced composites, and as an insulating material for wire and cables in nuclear power plants[12–14].

In our previous studies[2–7], the effects of gamma and electron beam (e.b.) irradiations on tensile properties, molecular motion and gas evolution for different aromatic polymers under different conditions were investigated. From these studies, it was revealed that PEEK possessed high radiation resistance and stability. It was concluded from the dynamic mechanical and X-ray diffraction measurements that PEEK crosslinked under non-oxidative conditions, but underwent chain scission in oxidative conditions.

The fact that a polymer with a rigid chain, such as PEEK, crosslinks on irradiation below its glass transition temperature (T_g) is a very interesting phenomenon. It is important to confirm this phenomenon by means of methods such as thermal analysis using d.s.c. which is a powerful technique. Knowledge of the changes in thermal properties of the polymer on irradiation is important for its applications in the field of aerospace systems and fusion reactors.

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EXPERIMENTAL

PEEK (PEEK-a, amorphous; PEEK-c, crystalline) was supplied by Mitsui Toatsu Chemicals Inc.

Irradiation

The film samples were irradiated under vacuum ($< 10^{-3}$ Pa) with ^{60}Co gamma rays at a dose rate of 10 kGy h^{-1} at room temperature (30°C).

Measurement of thermal properties

D.s.c. measurements were carried out using a Perkin-Elmer d.s.c. calorimeter equipped with a DSC-7 data station. Specimens (~ 7–8 mg) of the irradiated PEEK were used for d.s.c. measurements. Indium and zinc standards were utilized to calibrate the temperature and thermal scale. The measurements were carried out in N_2 atmosphere at a heating rate of 20°C min^{-1}. On first heating to 350°C, the specimen was held at this temperature for 5 min, and cooled to room temperature at a rate of 20°C min^{-1}. This process is referred to as the first cooling run. The heats of melting (ΔH_m), crystallization (ΔH_c) and recrystallization (ΔH_{rc}) of

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irradiated and unirradiated samples were determined from the area of the corresponding transitions in the d.s.c. scans. Isothermal crystallization of PEEK-a and PEEK-c was also performed using d.s.c. The specimens were heated to 350°C and held at this temperature for 10 min, before being cooled to a suitable isothermal crystallization temperature (T_{iso}) at a rate of 300°C min^{-1}. The heat flow for these samples was measured as a function of isothermal crystallization time ($t_{c,iso}$).

RESULTS AND DISCUSSION

Thermal properties

The crystallization temperature (T_c) was determined for PEEK-a from the first heating run and the recrystallization temperature (T_{rc}) was determined for PEEK-a and PEEK-c from the first cooling run. The T_g and melting temperature (T_m) for PEEK-a and PEEK-c were determined from the first and second heating runs.

The changes in T_g, T_c, T_{rc} and T_m with dose for PEEK-a and PEEK-c are shown in *Table 1*. The T_g of the unirradiated PEEK-c is higher than that of PEEK-a. This arises from the restriction of three-dimensional motion of chains in the non-crystalline domains of PEEK-c by the presence of crystallites. The T_g of PEEK-a shifts to higher temperatures on the second heating run as compared with the first heating, at a given dose. Since the second heating run was made for the specimen which had been cooled down from the molten state at a cooling rate of 20°C min^{-1}, the specimen had turned to a semicrystalline state. As a consequence, the T_g of PEEK-a on the second heating run is shifted to higher values compared to those for the first heating run, at a given dose.

The T_g for PEEK-c initially shifts to higher temperature with dose and then tends to level off at higher dose in both heating runs. The T_g for the unirradiated PEEK-c on the second run is lowered by 5°C compared to that of the first heating run. This is due to the decrease in its degree of crystallinity by cooling from the molten state at a relatively fast rate of 20°C min^{-1}.

It has been reported that H_2 evolution is a good indication of radiation-induced network formation which is strongly dependent on crystal morphology[15]. On irradiation, H_2 is evolved and radicals created; H_2 being the by-product and the radicals being the precursors of crosslink formation. In our previous studies[6,7], it was found that the G-value of H_2 for PEEK-a is almost twice that for PEEK-c on gamma and e.b. irradiations under vacuum. Accordingly, the behaviour of T_g for PEEK-c with dose on the first and second heating runs is little different from that of PEEK-a. This arises from the differences in the distribution and number of crosslinks in the two polymers. In PEEK-a these crosslinks are uniformly distributed and are in greater number than in PEEK-c. In the latter the crosslinks exist mainly in the non-crystalline domains.

The T_g is governed by the chemical structure of repeating units of the polymer, bulkiness, interaction of chains and presence or absence of crosslinks. In this case, it is reasonable to consider that the shift in T_g to higher temperature by irradiation is due to restriction of chain mobility caused by the crosslinking network structure formed on irradiation. It is well known that radiation has a significant effect on the amorphous region rather than on the crystalline region. While the radicals form uniformly throughout the whole polymer, they cannot form crosslinks in the rigid lattice, but do so in the amorphous polymer or amorphous regions of the semicrystalline polymer[16]. Changes in the amorphous regions are indicated by an increase in T_g with dose, which suggests that crosslinking is the more important radiation mechanism in PEEK.

The T_c on heating PEEK-a increases with dose, but the T_{rc} of PEEK-a and PEEK-c on cooling from the molten state decreases as the dose increases. This behaviour of T_c and T_{rc} with dose indicates clearly the occurrence of crosslinking. Consequently the crystallization by heating above T_g and recrystallization by cooling from the melt state are inhibited by such crosslinks. The T_c for PEEK-a slightly shifts to higher temperatures on irradiation, indicating that the thermal crystallization process is affected by radiation. The small difference in T_{rc} for PEEK-a and PEEK-c can be interpreted in terms of the difference in distribution of crosslinks in both polymers.

The T_m for both polymers decreases as the dose increases on the first and second heating runs. The decrease in T_m for PEEK-a is due to the inhibition of crystallization above T_g by the presence of crosslinks. In

Table 1 Effect of dose on the thermal properties of PEEK-a and PEEK-c

Polymer	Dose (MGy)	T_g (°C)		T_c (°C)	T_{rc} (°C)	T_m (°C)	
		First heating run	Second heating run			First heating run	Second heating run
PEEK-a	0	143	144	172	288	335	336
	3	144	146	174	284	332	334
	7.4	145	149	177	278	327	329
	15	146	151	182	267	319	322
	25	147	153	188	256	309	312
PEEK-c	0	151	146	–	295	335	337
	3.5	154	148	–	290	330	336
	8.1	155	149	–	283	326	322
	12.1	156	149	–	276	320	326
	15.6	157	150	–	271	316	320

Heating/cooling rate: 20°C min^{-1}

Table 2 Changes in ΔH_m, ΔH_c and ΔH_{rc} for PEEK-a and PEEK-c with irradiation dose

Polymer	Dose (MGy)	ΔH_m (J g^{-1}) First heating run	ΔH_m (J g^{-1}) Second heating run	ΔH_c (J g^{-1})	ΔH_{rc} (J g^{-1})
PEEK-a	0	33	29	21	40
	3	32	28	21	37
	7.4	30	26	21	35
	15	27	25	20	29
	25	25	24	19	23
PEEK-c	0	37	25	–	36
	3.5	36	28	–	36
	8.1	35	30	–	34
	12.1	32	29	–	33
	15.6	26	21	–	31

PEEK-c the decrease in T_m would result from the crosslinks of the chains in the interface between the non-crystalline and crystalline domains and/or the formation of defects in the polymer structure. The shift in T_m to higher values on the second heating run reflects the change in chain conformation of both polymers after being recrystallized on cooling from the molten state.

It has been reported that the temperature range of melting represents the distribution of the crystallite sizes present in the samples, and higher T_m values represent larger crystallite sizes (or greater perfection)[17]. It is known that the thermodynamic T_m of semicrystalline polymers decreases as the molecular weight decreases and/or as the number of defects increases, i.e. with an increase in branching and/or crosslinking[18,19]. Accordingly, the decrease in T_m on gamma irradiation indicates that there is a decrease in the size of crystallites and/or the formation of defects.

The changes in ΔH_m, ΔH_c and ΔH_{rc} in PEEK-a and PEEK-c with dose are shown in *Table 2*. The decrease in ΔH_m and ΔH_{rc} in PEEK-a and PEEK-c with increasing dose reflects the change in crystalline domains. The small change in ΔH_c of PEEK-a with dose indicates that the newly formed crystallites are hardly affected by radiation. The reduction in ΔH_m suggests that molecular changes in the crystalline regions are occurring. The decrease in T_m may also indicate a lower crystalline content due to the formation of crosslinks on irradiation. Therefore the decrease in T_m and ΔH_m for PEEK-a and PEEK-c is due to restriction of chain mobility and disordering of their structures caused by such crosslinks.

The decrease in T_{rc} and ΔH_{rc} on gamma radiation is good evidence of crosslink formation in the PEEK structure, since crosslinking decreases the crystallizability of the polymer[20]. The decrease in ΔH_{rc} with dose for PEEK-c is less than that for PEEK-a due to the lower probability of crosslinking in the crystalline domains in PEEK-c. The degree of crosslinking increases as the dose increases[21] in both polymers, consequently the restriction of the recrystallization process in PEEK is enhanced at higher doses.

Isothermal crystallization

The above results show that radiation has significant effects on the crystallization and recrystallization processes in PEEK. The influence of radiation on the isothermal crystallization of PEEK-a and PEEK-c is shown in *Figures 1–6*. *Figure 1* shows a typical d.s.c.

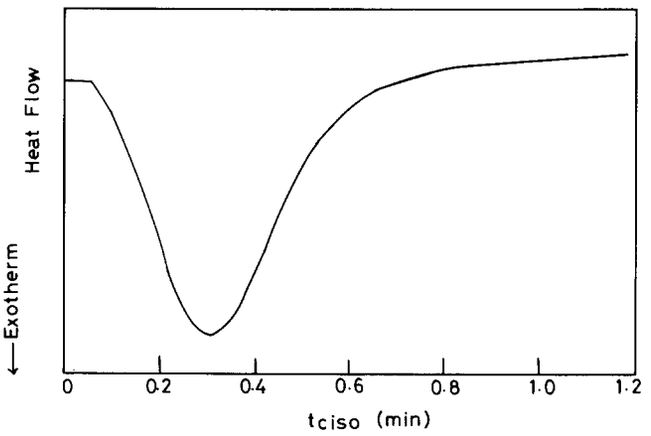

Figure 1 Typical d.s.c. diagram of isothermal crystallization for PEEK-c irradiated at 3.5 MGy. Crystallization temperature: 290°C

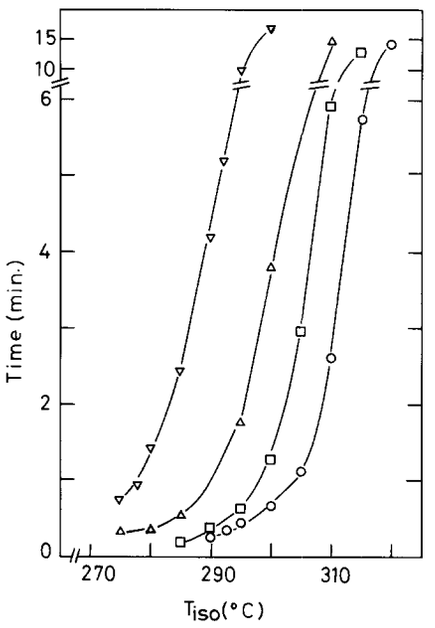

Figure 2 Plot of $t_{c,iso}$ *versus* T_{iso} for PEEK-a at different doses (MGy); (○) 0; (□) 2.9; (△) 7.4; (▽) 15

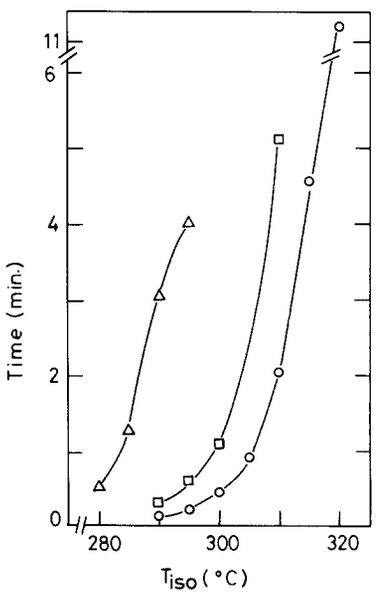

Figure 3 Plot of $t_{c,iso}$ *versus* T_{iso} for PEEK-c at different doses (MGy); (○) 0; (□) 3.5; (△) 15.6

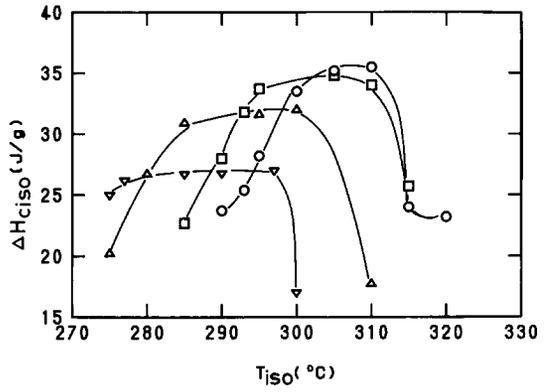

Figure 4 Plot of $\Delta H_{c,iso}$ *versus* T_{iso} for PEEK-a at different doses (MGy); (○) 0; (□) 2.9; (△) 7.4; (▽) 15

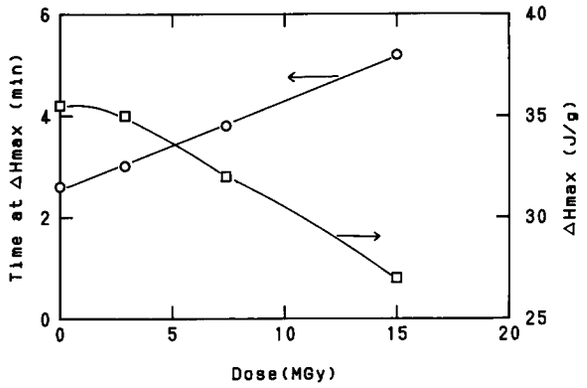

Figure 5 Effect of dose on $t_{c,iso}$ and maximum $\Delta H_{c,iso}$ for PEEK-a

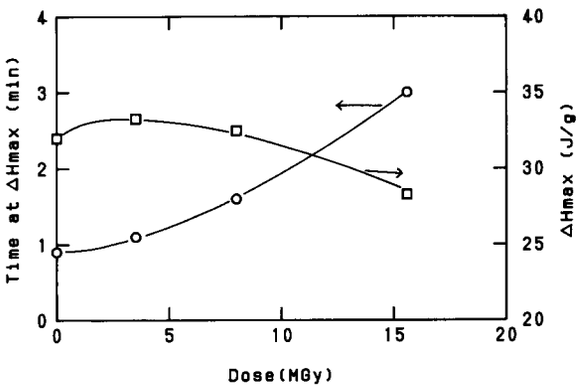

Figure 6 Effect of dose on $t_{c,iso}$ and maximum $\Delta H_{c,iso}$ for PEEK-c

diagram of isothermal crystallization for PEEK-c irradiated at 3.5 MGy and crystallized isothermally at 290°C. The heat flow decreases with time, showing a minimum, and then increases again. The rate of crystallization is a maximum at the time of the peak. (This is defined as $t_{c,iso}$.)

Figures 2 and *3* show $t_{c,iso}$ as a function of T_{iso} for PEEK-a and PEEK-c at different doses, respectively. In the temperature and time ranges of this study, the unirradiated PEEK-a and PEEK-c give the shortest $t_{c,iso}$ at 290°C and it increases as T_{iso} increases. The $t_{c,iso}$ shifts to lower T_{iso} as the dose increases for both polymers, indicating that the isothermal crystallization process is also inhibited by irradiation due to the formation of crosslinks.

Figure 4 shows the heat of crystallization obtained isothermally ($\Delta H_{c,iso}$) as a function of T_{iso} for PEEK-a at different doses. The T_{iso}, at which the maximum $\Delta H_{c,iso}$ is obtained, decreases as the dose increases. The effect of dose on $t_{c,iso}$ and maximum $\Delta H_{c,iso}$ for PEEK-a and PEEK-c is shown in *Figures 5* and *6*, respectively. The $t_{c,iso}$ increases but maximum $\Delta H_{c,iso}$ decreases with increasing dose for both polymers. The increase in time giving maximum $\Delta H_{c,iso}$ and the decrease in $\Delta H_{c,iso}$ per dose for PEEK-c are lower than those of PEEK-a. This can be attributed to the degree and distribution of crosslinks which are higher and more uniformly distributed in PEEK-a as discussed earlier.

CONCLUSIONS

D.s.c. results have shown that radiation has a significant effect on the crystallization and recrystallization behaviours of PEEK. Results indicate that crosslinking is the main radiation mechanism for PEEK on gamma irradiation under vacuum. This leads to an increase in T_g and decrease in both T_m and T_{rc} as the dose is increased. The decrease in temperature and heat of recrystallization of PEEK on irradiation is good evidence of crosslink formation, since crosslinking decreases the crystallizability of the polymer. Results from the isothermal crystallization of PEEK-a and PEEK-c confirmed that the crosslinks in PEEK greatly restrict chain mobility and crystallization.

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