Radiation deterioration of several aromatic polymers under oxidative conditions

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Radiation-induced oxidative irradiation effects (with γ-rays under oxygen pressure) or poly(aryl sulphones) (U-PS and PES), poly(aryl ester) (U-Polymer), poly(aryl amide) (A-Film) and poly(aryl ether ether ketone) (PEEK) have been studied based on changes in tensile properties. The deterioration dose estimated from the decrease in the elongation at break was as low as one-fifth to one-tenth of that in high-dose-rate electron-beam irradiation, but the order of radiation resistance of the polymers did not differ from that in electron-beam irradiation, i.e. PEEK > A-Film > U-Polymer > U-PS > PES. The radiation stability of aromatic units under oxidative conditions was estimated from a comparison of the radiation resistance of the polymers themselves and their chemical structures. The following order was obtained: diphenyl ether, diphenyl ketone > aromatic amide $\gg$ bisphenol A > diphenyl sulphone. The deterioration mechanism of PEEK under oxidative irradiation was studied by measuring dynamic viscoelastic properties. It was concluded that deterioration in mechanical properties under oxidative irradiation was brought about by chain scission only.

(Keywords: aromatic polymers; oxidative irradiation; mechanical properties; viscoelastic properties; chain scission)

INTRODUCTION

Some attention has been paid to the use of aromatic polymers composed of various functional aromatic units in the main chain as high-performance engineering plastics. These polymers are expected to find use in high radiation fields, such as around fast-neutron breeder piles, fusion reactors and in space, because aromatic compounds are believed to be stable to radiation. We have already reported that aromatic polymers show high resistance compared with aliphatic polymers for high-dose-rate electron-beam irradiation, but the radiation resistance depends strongly on their chemical structures[1].

It is known that radiation-induced oxidation takes place when polymers are irradiated in an atmosphere containing oxygen. For instance, in the case of irradiation by γ-rays with very low dose rate in air for long periods, polymer material is oxidized right to the inside[2]. On the other hand, in high-dose-rate electron-beam irradiation, only a very thin layer of material is oxidized, because the oxygen is consumed in a thin layer on the surface of the material before it diffuses into the inside. The deterioration behaviour of aromatic polymers reported previously[1] can be regarded as equivalent to deterioration by irradiation in vacuum.

Polymer materials are often used in irradiation environments accompanied by oxidative reaction, so that knowledge of irradiation effects under oxidative conditions is important. Irradiation at very low dose rates, however, is impracticable, because a very long time is required to evaluate radiation effects. Seguchi *et al.*[2] proposed a new technique to enable oxidation to proceed well inside the polymer material under relatively high-dose-rate irradiation (1×10^4 Gy h^{-1}). This technique is characterized by irradiation under an oxygen pressure to promote diffusion of oxygen to the inside of the material.

In this paper, radiation deterioration of the mechanical properties of several aromatic polymers under oxidative conditions has been studied using the new technique. Further, the deterioration mechanism in oxidative irradiation was discussed for poly(aryl ether ether ketone) (PEEK) based on changes in molecular motion.

EXPERIMENTAL

The polymers used are poly(aryl ether sulphone) (PES), a bisphenol A type poly(aryl sulphone) (Udel-polysulfone, U-PS), poly(aryl ester) U-Polymer), poly(aryl amide) (A-Film) and poly(aryl ether ether ketone) (PEEK). The samples of PES and PEEK were kindly supplied by Sumitomo Chemical Co. Ltd, U-PS was obtained from Toray Industries Inc., and U-Polymer and A-Film were from Unitika Co. Ltd, as sheets with about 0.1 mm thickness. PEEK was received in the non-crystalline state (PEEK-a) and it was used as the sample of a non-crystalline state. The sample of semicrystalline PEEK (PEEK-c) was prepared by heat treatment of PEEK-a at 200°C for 30 min. The degree of crystallinity was measured to be about 15% by X-ray diffraction. The non-crystalline PEEK samples for viscoelastic measurements were prepared by high-speed quenching from 360°C to room temperature after re-formation into a sheet with 0.5 mm thickness in a hot press. The semicrystalline PEEK samples were obtained by heat treatment of the non-crystalline sheet at 200°C for 30 min.

Irradiation was carried out on specimens in the shape of JIS No. 4 dumbbell using ^{60}Co γ-rays. Two irradiation conditions were employed: (1) dose rate of 5×10^3 Gy h^{-1} under 0.7 MPa oxygen pressure; (2) dose rate of 1×10^4 Gy h^{-1} in air. Irradiation was at room temperature for both sets of conditions.

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The tensile tests were performed at 25°C with a crosshead speed of 200 mm min^{-1}. The Young's modulus is obtained from the initial slope of the stress–strain curves; the yield strength is calculated from the maximum stress just after yielding; the tensile strength at break was obtained from the stress at break; and the elongation was determined by dividing overall displacement at break by the initial length of the dumbbell neck (30 mm). These tensile parameters are represented by the average and standard deviation of five specimens.

The viscoelastic properties were measured on strips with dimensions of 0.5 mm thickness × 10 mm width × 100 mm length by use of a torsion-pendulum-type apparatus (Rescha RD 1100AD) in the temperature range −160 to 320°C at a frequency of 0.2–1 Hz. The viscoelastic measurements were performed after the specimens were dried on silica gel in vacuum, in order to avoid the influence of small amounts of water molecules on the low-temperature relaxation.

RESULTS AND DISCUSSION

Evaluation of oxidation conditions

The thickness of the oxidized layer is controlled by the diffusion constant of oxygen (D), the solubility of oxygen in the material (S), the dose rate and the G value of radical formation. It has been reported that polyethylene and polypropylene with 1 mm thickness can be oxidized well inside the surface by irradiation at a dose rate of 1×10^4 Gy h^{-1} under 0.5 MPa oxygen pressure[2].

The reported values[3] of D and S for polyethylene and polypropylene are $D=(3\text{–}9)\times 10^{-7}\,cm^2\,s^{-1}$, $S=(1\text{–}5)\times 10^{-6}\,mol\,g^{-1}\,atm^{-1}$. The values for PES, U-Polymer and the polyimide 'Kapton' measured by the same method are as follows: $D=1.55\times 10^{-8}\,cm^2\,s^{-1}$, $S=4.72\times 10^{-6}\,mol\,g^{-1}\,atm^{-1}$ for PES; $D=4.98\times 10^{-8}\,cm^2\,s^{-1}$, $S=8.03\times 10^{-6}\,mol\,g^{-1}\,atm^{-1}$ for U-Polymer; and $D=2.32\times 10^{-9}\,cm^2\,s^{-1}$, $S=3.98\times 10^{-6}\,mol\,g^{-1}\,atm^{-1}$ for Kapton, respectively. The data obtained show that the diffusion constants of oxygen for aromatic polymers are one to two orders lower than those of aliphatic polymers but that the solubility of oxygen is comparable to those of aliphatic polymers.

The G value of radical formation of aromatic compounds, in general, is less than that of aliphatic compounds; for example[4], the G value of total radical formation for phenoxyphenoxydiphenyl is about 0.04 and that for n-alkane is 2.5. Thus, the diffusion constant of aromatic polymers is one or two orders smaller than that of aliphatic polymers, and the G value of radical formation is about two orders smaller compared with aliphatic polymers. Further, the solubility of oxygen is of the same order as that for aliphatic polymers. Consequently, the irradiation conditions in the present work (5×10^3 Gy h^{-1} under 0.7 MPa oxygen pressure for polymers with 0.1 mm thickness) are sufficient to oxidize materials right to the inside.

Radiation stability of aromatic units in oxidative irradiation

Irradiation in air. *Table 1* gives the relations between tensile parameters and dose for irradiation in air. *Table 2* shows the same relations for irradiation under 0.7 MPa oxygen pressure. From the two tables, the following changes are seen: with increasing dose, (1) the Young's modulus tends to increase, (2) the tensile strength and

Table 1 Tensile properties of aromatic polymers irradiated by γ-rays in air

Polymer	Dose (MGy)	Young's modulus (GPa)	Yield stress (MPa)	Tensile stress (MPa)	Elongation (%)
PEEK-a	0	1.17±0.08	73.3±1.2	132.3±13.9	286±33
	4.9	1.15±0.11	71.4±1.4	104.6±3.3	280±13
	9.8	1.15±0.14	75.4±1.3	92.2±3.6	252±18
	19.5	1.50±0.05		81.6±1.9	15±11
	29.1	1.49±0.08		66.0±8.3	5±1
PEEK-c	0	1.37±0.07	97.4±1.7	97.0±8.0	175±33
	4.9	1.46±0.09	96.3±1.8	81.0±2.1	176±20
	9.8	1.67±0.07	97.5±1.8	62.3±1.4	20±13
	19.5	1.71±0.10		68.2±9.8	4±1
Polyamide (A-Film)	0	2.29±0.06	125.6±10.8	147.9±1.2	186±7
	2.1	2.03±0.11	144.2±5.4	161.5±9.3	183±11
	4.0	2.15±0.16	147.7±1.0	156.3±7.6	145±25
	8.2	2.30±0.15	146.1±0.3	143.6±2.4	136±36
	15.3	2.45±0.05	143.9±4.7	118.1±5.6	39±10
Polyester (U-Polymer)	0	1.06±0.03	73.7±1.1	75.7±1.2	88±10
	0.45	1.11±0.05	74.7±0.7	69.1±2.5	41±11
	0.91	1.17±0.01	74.5±0.6	68.2±2.1	19±5
	1.5	1.19±0.11	72.7±1.9	65.9±2.7	25±11
	3.0	1.02±0.01	72.6±0.6	68.6±1.8	16±1
	5.7	1.17±0.18		35.4±5.5	3±0.3
Polysulphone (Udel)	0	1.20±0.07	84.2±1.2	84.8±1.9	235±4
	0.23	1.21±0.11	78.3±0.5	78.5±2.1	192±9
	0.62	1.30±0.07	77.9±1.6	67.6±3.3	142±22
	0.91	1.42±0.05	78.9±0.6	60.7±2.1	67±29
	1.6	1.29±0.05	77.9±1.2	60.3±3.8	14±6
Polysulphone (PES)	0	1.36±0.08	89.8±1.3	81.6±6.9	175±5
	0.23	1.31±0.12	87.3±1.5	79.3±5.7	156±27
	0.62	1.52±0.10	91.2±1.0	68.3±0.5	39±11
	0.91	1.59±0.03	89.5±0.2	65.5±1.0	19±4
	1.6	1.43±0.10	89.5±8.5		7±2

Table 2 Tensile properties of aromatic polymers irradiated by γ-rays under 0.7 MPa oxygen

Polymer	Dose (MGy)	Young's modulus (GPa)	Yield stress (MPa)	Tensile stress (MPa)	Elongation (%)
PEEK-a	0	1.17±0.07	73.3±1.2	132.2±13.9	296±33
	2.1	1.38±0.10	77.5±2.9	115.3±4.3	273±9
	4.0	1.36±0.17	76.0±2.1	104.3±3.0	260±10
	8.1	1.48±0.10	76.3±1.5	73.5±2.9	181±23
	11.8	1.17±0.05		85.5±1.1	15±9
PEEK-c	0	1.37±0.07	97.4±1.7	97.0±8.0	175±33
	2.1	1.59±0.15	99.9±1.9	75.4±1.9	67±7
	4.0	1.73±0.09	99.5±2.1	72.3±3.8	48±13
	8.1	1.91±0.14	98.9±0.6	77.3±10.8	14±3
Polyamide (A-Film)	0	2.29±0.06	125.6±1.1	147.9±1.2	186±7
	2.1	2.26±0.15	142.7±2.4	125.9±18.6	130±25
	4.0	2.24±0.14	145.4±2.5	143.7±2.5	133±32
	8.1	2.58±0.10		115.1±5.3	5±0.3
Polyester (U-Polymer)	0	1.06±0.03	73.7±1.1	75.7±1.2	88±10
	0.25	0.95±0.04	73.5±0.4	68.7±2.1	45±17
	0.34	1.04±0.03	74.9±2.1	69.8±2.6	47±10
	0.53	1.55±0.35	72.5±0.3	64.7±1.4	16±2
Polysulphone (Udel)	0	1.02±0.07	84.2±1.2	84.8±1.9	235±4
	0.25	1.16±0.05	78.5±3.6	63.6±0.9	120±36
	0.53	1.23±0.04	77.9±0.5	58.9±2.1	51±30
Polysulphone (PES)	0	1.36±0.08	89.8±1.3	81.6±1.3	175±5
	0.25	1.38±0.13	88.5±10	60.5±0.6	54±13
	0.53	1.31±0.09	88.2±2.7	63.8±0.8	14±3

elongation at break decrease, but (3) the change in yield strength is minor. Since, among the changes in tensile parameters, decrease in elongation is the most susceptible to irradiation, the degree of deterioration was evaluated based on decrease in elongation.

The elongation at break is shown as a function of dose in *Figures 1* to *6* together with the results from electron-beam irradiation[1]. In these figures the elongation is represented by the value normalized by that of the unirradiated specimen (residual elongation). The relations between the residual elongation and dose under irradiation in air for U-PS, PES and U-Polymer resemble those in electron-beam irradiation. This indicates that oxidative deterioration takes place in only a thin surface layer for a short period (maximum 20 days) even for γ-ray irradiation in air.

The decrement in elongation of A-Film against dose during irradiation in air is slightly larger than that in electron-beam irradiation, but A-Film keeps a relatively high elongation for a long period (65 days), indicating that the diffusion constant of oxygen would be fairly small.

The residual elongation for PEEK-a and PEEK-c initially is scarcely changed and then decreases sharply in the high-dose region (above 3 MGy for PEEK-c and 15 MGy for PEEK-a). As reported previously[4], crosslinking and chain scission take place simultaneously in PEEK under high-dose-rate electron-beam irradiation. In γ-ray irradiation in air, chain scission should occur mainly on the surface and crosslinking should occur mainly inside the polymer. Less change in elongation in the initial stages would be brought about by a balance between scission on the surface and crosslinking inside the material. The sharp decrease in elongation in the high-dose region may be caused by enlargement of the oxidized layer to the inside for long-period irradiation (15 days for PEEK-c, 76 days for PEEK-a).

The dose giving rapid decrease in elongation for PEEK-c is lower than for PEEK-a. Also in electron-beam

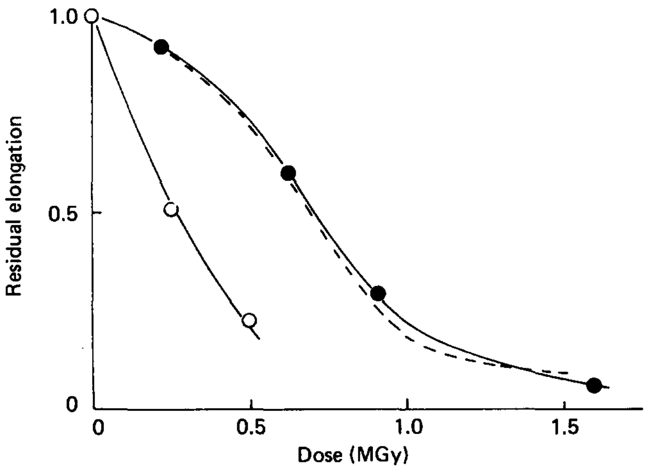

Figure 1 Residual elongation as a function of dose for U-PS: ●, γ-rays in air; ○, γ-rays under 0.7 MPa oxygen; -----, electron beam in air

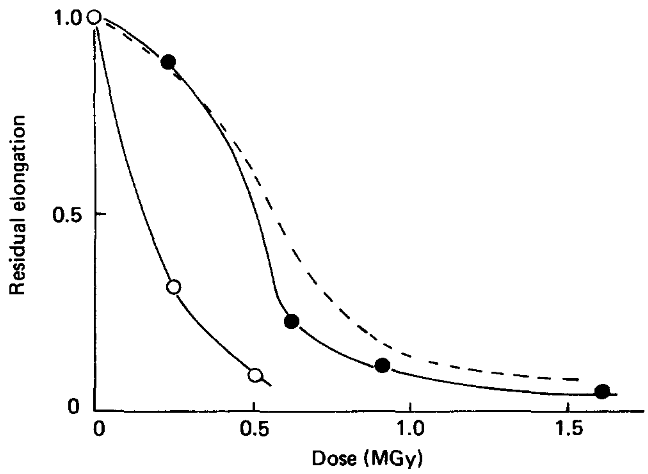

Figure 2 Residual elongation as a function of dose for PES: notation as in *Figure 1*

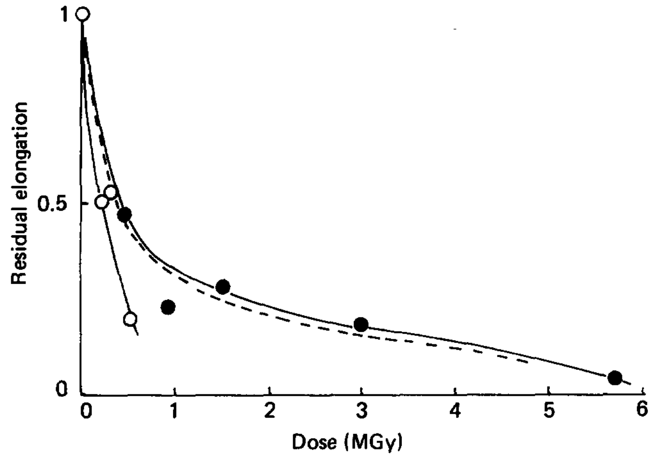

Figure 3 Residual elongation as a function of dose for U-Polymer: notation as in *Figure 1*

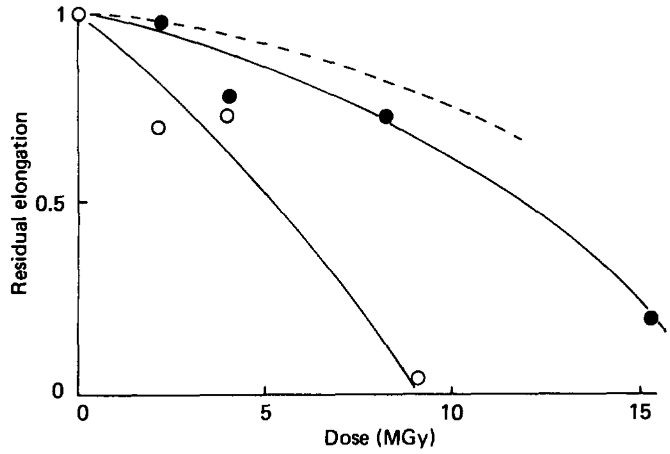

Figure 4 Residual elongation as a function of dose for A-Film: notation as in *Figure 1*

irradiation, PEEK-c shows a lower radiation resistance than PEEK-a. It has been reported that the chains existing at the interface between crystalline and non-crystalline domains are affected more by irradiation than chains in non-crystalline and/or crystalline phases[5]. The difference in deterioration doses between PEEK-a and PEEK-c increases in comparison with that in electron-beam irradiation. The diffusion constant of oxygen might be increased by partial crystallization.

Irradiation under oxygen pressure. In the irradiation under oxygen pressure, elongation of all polymers decreases markedly with increasing dose. This is the result of radiation-induced oxidation right to the inside of the polymers. The doses which make the elongation decrease to half of the initial value under oxidative irradiation are 0.25 MGy for U-PS, 0.2 MGy for PES, 0.35 MGy for U-Polymer, 5 MGy for A-Film, 1.5 MGy for PEEK-c and 9 MGy for PEEK-a, respectively. The order of radiation resistance of polymers can be evaluated as follows: PEEK-a > A-Film > PEEK-c ≫ U-Polymer > U-PS > PES.

Radiation effects should be affected not only by chemical structure but also by higher-order structure such as the presence or not of crystallites, because the chain conformation and molecular motion may have a large influence on reactivity of the active species produced by irradiation. Therefore, evaluation of the radiation stability of the aromatic unit should be done under conditions in which the effects of crystallinity can be excluded. The polymers used in the present work are non-crystalline polymers, except PEEK-c, so that the order of stability of the aromatic units is deduced on the polymers, except for PEEK-c.

The relation between radiation resistance and chemical structure under oxidative radiation can be summarized as follows:

(1) The two polysulphones show the lowest resistance, so that diphenyl sulphone is not stable under oxidative irradiation.

(2) U-PS and U-Polymer, which contain bisphenol A groups, are not stable, indicating that the structure of bisphenol A also has low resistance against oxidative irradiation.

(3) Since A-Film shows a relatively high resistance, the aromatic amide group is a relatively resistant structure for oxidative irradiation.

(4) Non-crystalline PEEK shows high resistance, indicating that diphenyl ether and ketone have high stability for oxidative irradiation.

From the comparison, we propose the following order of radiation stability of aromatic units under oxidative conditions: diphenyl ether, diphenyl ketone > aromatic amide ≫ bisphenol A > diphenyl sulphone. The radiation resistance of these polymers for oxidative irradiation is lower than for electron-beam irradiation but the order of stability of the aromatic units under oxidative conditions

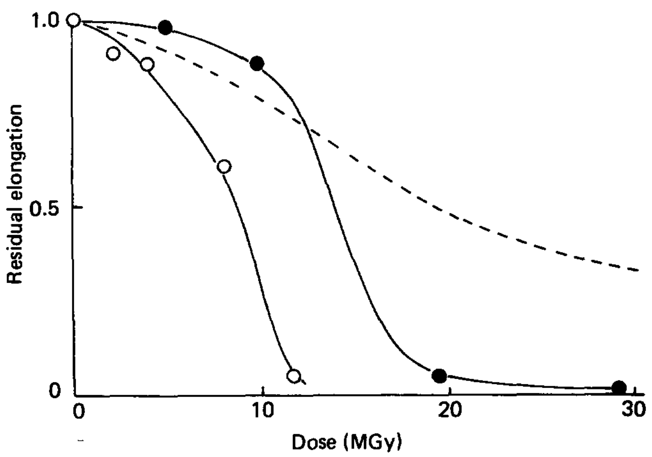

Figure 5 Residual elongation as a function of dose for PEEK-a: notation as in *Figure 1*

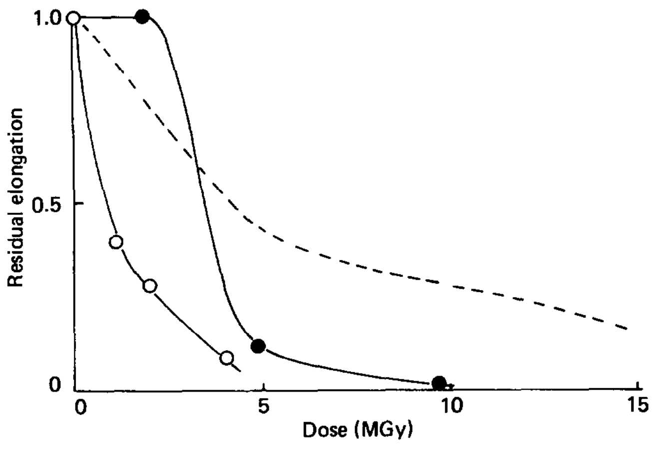

Figure 6 Residual elongation as a function of dose for PEEK-c: notation as in *Figure 1*

seems to be the same as in high-dose-rate electron-beam irradiation.

Mechanism in deterioration of PEEK under oxidative irradiation

Figure 7 shows the temperature dependence of logarithmic decrement (*Figure 7a*) and dynamic shear modulus (*Figure 7b*) for the non-crystalline PEEK unirradiated and irradiated with 12 MGy under oxidative conditions. Three discrete mechanical loss peaks are observed at −80, 150 and 180°C for the unirradiated specimen. These mechanical losses are named γ, β and α' relaxations from low to high temperature. The low-temperature relaxation (γ relaxation) in rigid aromatic polymers is generally assigned to local motion of aromatic units in the main chain in the glassy state[5–7]. The β relaxation is attributable to molecular motion reflecting the transition from glassy to elastic state, because the shear modulus decreases sharply at the same temperature. The shear modulus increases again above the glass transition temperature. It is known that non-crystalline PEEK changes to a semicrystalline polymer on heat treatment above the glass transition temperature[8–10], so that an increase in shear modulus above the glass transition temperature should be brought about by crystallization. Therefore the α' relaxation can be assigned as molecular rearrangement from non-crystalline to semicrystalline state.

It was observed in electron-beam irradiation[11] that the β and α' relaxation peaks shift to higher temperature and the magnitude of the α' relaxation is lowered with increasing dose. The shift of the α' relaxation peak to higher temperature and its decreasing magnitude indicate the appearance of a structure inhibiting crystallization. We concluded, judging from the shift of the glass transition to higher temperature, that a crosslinking structure is introduced by high-dose-rate electron-beam irradiation.

In contrast with electron-beam irradiation, the peaks of the β and α' relaxations shift to lower temperature and the intensity of the α' relaxation peak is enhanced by oxidative irradiation. The shift of the α' relaxation peak to lower temperature shows that crystallization occurs easily at lower temperature. Accompanied by enhancement of the intensity of the α' relaxation, the shear modulus above 180°C increases on irradiation. This shows that the degree of crystallinity increases. These changes in mechanical relaxation should be interpreted in terms of a lowering of molecular weight by chain scission. Further, the lowering of the glass transition temperature might support the lowering of molecular weight.

A new relaxation appears as a shoulder just below the glass transition temperature (β' relaxation). This relaxation is often observed in irradiated polymers having a high glass transition temperature. From the experiments on annealing and high-speed quenching of several aromatic polymers[11–15], the β' relaxation was assigned to movement of the main chains during rearrangement from a loosened chain packing to a more rigid chain packing. The appearance of the β' relaxation on irradiation results from the disturbance of molecular packing caused by chain ends created by radiation-induced chain scission. Consequently, it can be concluded

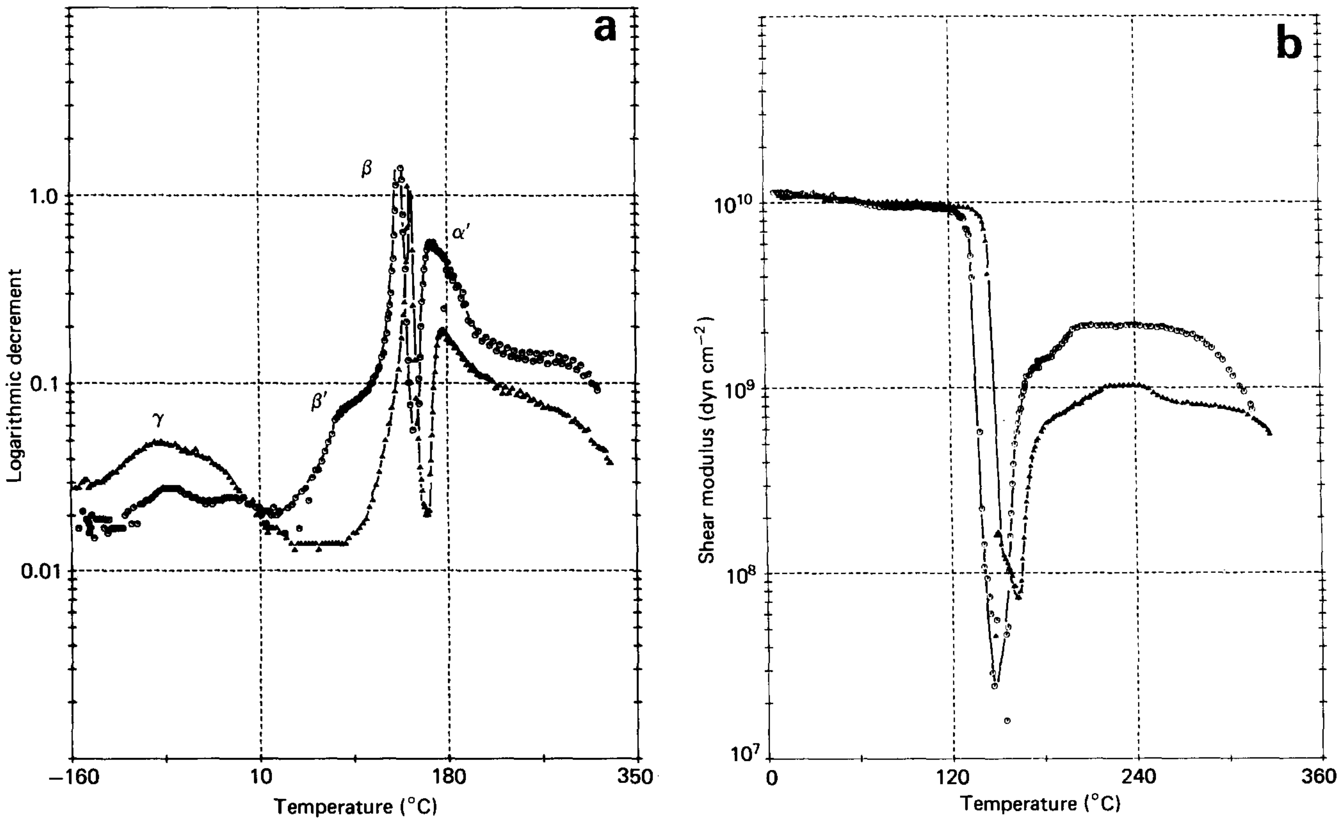

Figure 7 (a) Temperature dependence of logarithmic decrement for non-crystalline PEEK irradiated by γ-rays under 0.7 MPa of oxygen pressure: ▲, unirradiated; ○, irradiated with 12 MGy. (b) Temperature dependence of dynamic shear modulus for non-crystalline PEEK irradiated by γ-rays under 0.7 MPa of oxygen pressure: ▲, unirradiated; ○, irradiated with 12 MGy

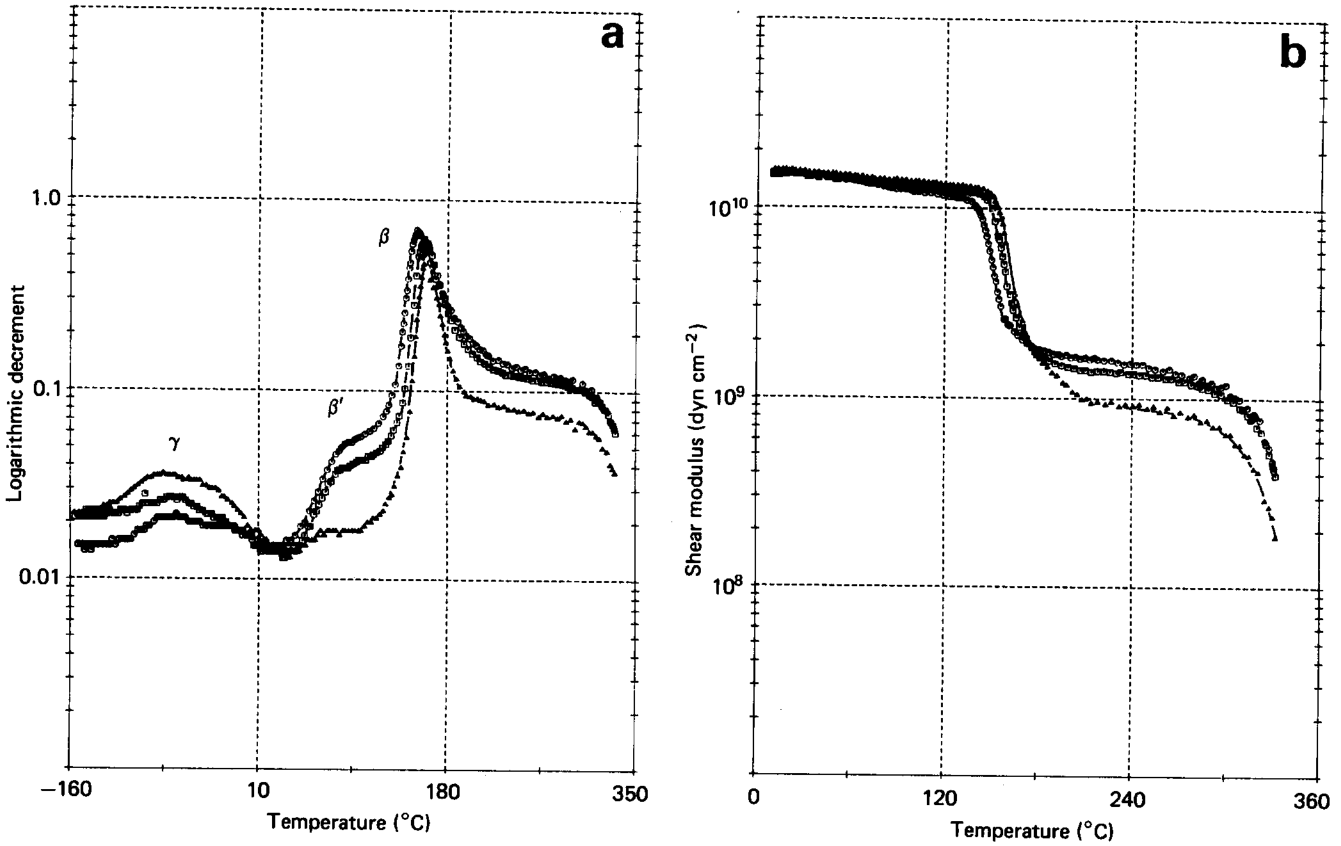

Figure 8 (a) Temperature dependence of logarithmic decrement for semicrystalline PEEK irradiated by γ-rays under 0.7 MPa of oxygen pressure: ▲, unirradiated; □, irradiated with 4 MGy; ○, irradiated with 8 MGy. (b) Temperature dependence of dynamic shear modulus for semicrystalline PEEK irradiated by γ-rays under 0.7 MPa oxygen pressure: ▲, unirradiated; □, irradiated with 4 MGy; ○, irradiated with 8 MGy

from the changes in the β and α' relaxations and the appearance of the β' relaxation that vigorous deterioration in tensile properties of PEEK irradiated under oxidative conditions is mainly due to chain scission.

Figures 8a and *8b* show the same relations for semicrystalline PEEK irradiated with various doses. In these figures, the α' relaxation is not observed, because crystallization has already been completed. Also in the case of semicrystalline PEEK, a shift of the glass transition to lower temperature, an increase in intensity of the β' relaxation and an increase in shear modulus above the glass transition temperature are observed with increasing dose. These results show clearly that chain scission occurs, as in non-crystalline PEEK.

As seen in *Figures 7a* and *8a*, the behaviour in the γ relaxation region is changed markedly by irradiation. The detailed γ relaxation spectra of semicrystalline PEEK are shown in *Figure 9*. The γ relaxation of the unirradiated specimen can be seen to be composed of two components: the main peak at about −75°C, responsible for the local motion of the main chain in the glassy state, and a shoulder in the temperature range −40 to 0°C. In electron-beam irradiation[12], the magnitude of the shoulder decreases with dose and the shoulder appears again in the second run. This result was interpreted as a moiety having a specific chain conformation damaged by irradiation and reproduced during recrystallization after the first run. The shoulder is assigned to molecular motion of chains existing at the interface between crystalline and non-crystalline domains.

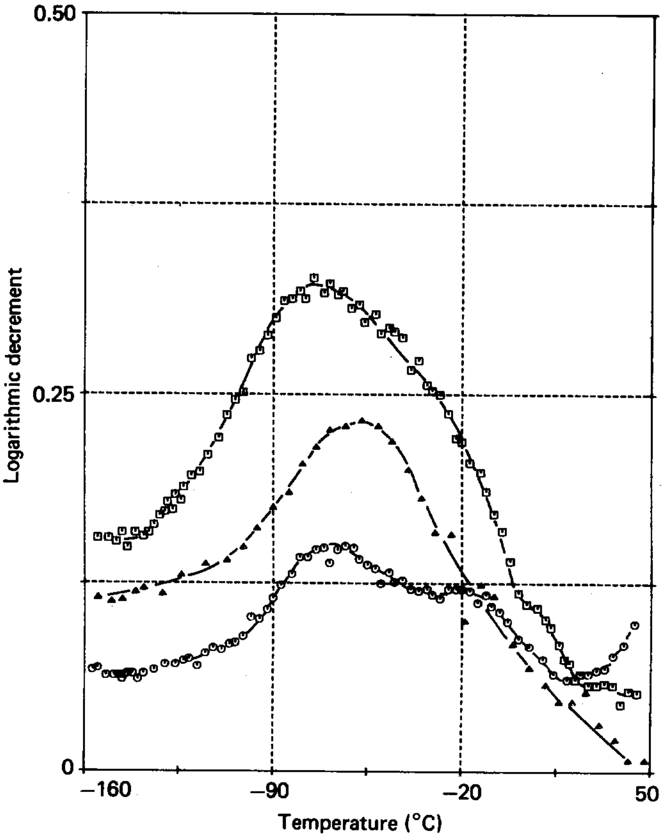

Figure 9 Detailed changes in the γ relaxation region for semicrystalline PEEK: □, unirradiated; ○, irradiated with 8 MGy under oxidative conditions; ▲, the second run for the irradiated specimen

In oxidative irradiation, the decrease in the magnitude of the γ relaxation is marked in comparison with the electron-beam irradiation, and even in the second run the peak profile differs from that of the unirradiated specimen. This indicates that damage to chains in the non-crystalline phase is vigorous and that the chain conformation at the interface between crystalline and non-crystalline domains for the specimen recrystallized after being irradiated under oxidative conditions differs from that of the unirradiated specimen. It can be considered that recrystallization is affected by changes in first-order structure, such as formation of an oxidized moiety during irradiation. Marked changes in the γ relaxation region indicate the occurrence of considerable damage to the chemical structures.

Finally, from the changes in tensile properties and molecular motions, characteristics in oxidative irradiation are summarized as follows: (1) aromatic polymers which show relatively high radiation resistance for non-oxidative irradiation deteriorate vigorously under oxidative irradiation—the deterioration dose is as low as one-fifth to one-tenth of that in high-dose-rate electron-beam irradiation; (2) the vigorous deterioration is brought about mainly by chain scission.

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