Mechanical relaxation of crystalline poly(aryl-ether-ether-ketone) (PEEK) and influence of electron beam irradiation

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Mechanical relaxation of semicrystalline PEEK and influence of electron beam irradiation on molecular motions were studied by measuring dynamic viscoelastic properties in the temperature range from −160°C to 350°C. Irradiation caused the glass transition temperature (β relaxation) to shift upwards, and β' relaxation, related to loosened chain packing, to appear just below the glass transition temperature, and a small shoulder that appeared at −40°C to 0°C on the γ relaxation peak and disappeared in the first run after irradiation to reappear in the second run. It was concluded that both crosslinking and chain scission take place under irradiation. The shoulder on the γ relaxation was assigned to segmental motion of the chains at the crystalline–non-crystalline interface. The inferior radiation resistance of semicrystalline PEEK with respect to non-crystalline PEEK is ascribed to preferential disintegration of tie-molecules between crystalline and non-crystalline phases.

(Keywords: semicrystalline PEEK; molecular motions; electron beam irradiation; chain scission; crosslinking; crystalline–non-crystalline interface)

INTRODUCTION

Recently, poly(aryl-ether-ether-ketone) (PEEK) has received attention as a high temperature engineering thermoplastic. Non-crystalline PEEK can be prepared by rapid quenching from the melt and semicrystalline PEEK can be obtained by annealing above the glass transition temperature (~150°C)[1-4]. Usually PEEK is used in the semicrystalline state, because crystalline PEEK has better mechanical properties than non-crystalline PEEK.

Non-crystalline PEEK showed higher resistance than semicrystalline PEEK to electron irradiation[5] of high dose rate. The polymer chains in crystallites are said to be more stable to irradiation than those in the non-crystalline phase[6-8]. The difference in radiation susceptibility between non-crystalline and crystalline chains would result partly from a different in freedom of molecular motion between the phases, because suitable molecular motion is required for chain scission or crosslinking, or both. In the crystalline phase, molecular motion is largely restricted by the crystal lattice, so that the probability of chain scission and crosslinking is less than in the non-crystalline phase. Therefore, the chains in crystallites can be considered to be less susceptible to irradiation than those in the non-crystalline phase. Simple application of the concept suggests that semicrystalline PEEK should be more resistant than non-crystalline to irradiation. However, the experimental results show the opposite order of radiation stability as evaluated by degradation of mechanical properties[5]. Lower radiation resistance of semicrystalline PEEK seems to be influenced by irradiation susceptibility of molecules in another region, for example, the interface between crystalline and non-crystalline phases.

In this paper, electron beam irradiation effects on molecular motions revealed by viscoelastic measurements of semicrystalline PEEK were investigated. The difference in deterioration mechanism between semicrystalline and non-crystalline PEEK is discussed.

EXPERIMENTAL

Semicrystalline sheet sample, 1 mm thickness, was kindly supplied by Sumitomo Kagaku Kogyo Co. Ltd. The polymer was reformed to a sheet of ~0.5 mm thickness in a hot press at 360°C and was quenched to room temperature. This treatment converted the PEEK to a non-crystalline transparent sheet. Crystallization was performed by heating at 200°C for 30 min. The degree of crystallinity was ~15% by X-ray diffraction.

Irradiation was carried out in an electron beam at a dose rate of $5 \times 10^3\ \mathrm{Gy\ s^{-1}}$ (acceleration voltage, 2.0 MeV; current, 1.5 mA) on a stainless steel plate with cooling water jacket to prevent raising the temperature of the polymer during irradiation. The dynamic viscoelastic properties were measured on $100 \times 10 \times 0.5$ mm strips in the temperature range of −160°C to 320°C by a torsion pendulum type apparatus (RHESCA RD 1100AD), frequency range 0.2–1 Hz.

As reported previously, the peak temperature and magnitude of the low temperature relaxation (γ relaxation peak appearing at about −100°C) is affected by traces of absorbed water; to remove this effect, all specimens were dried with silica gel in vacuum for 7 days before viscoelastic measurement.

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RESULTS

Figure 1 shows temperature dependence of shear modulus (G') and logarithmic decrement (mechanical loss) of non-irradiated semicrystalline PEEK during the first and second runs. Two discrete mechanical loss peaks, γ and β relaxations, are observed. In the first run, a small β' relaxation is observed in the range 40–110°C, between the γ and β relaxations. The loss in this range becomes very small in the second run after the thermal experience in the first run. A marked decrease in shear modulus occurs above 320°C in both runs.

In *Figure 2* temperature dependence of mechanical loss is compared for non-irradiated polymer and polymer irradiated with 30 MGy. After irradiation the γ relaxation peak becomes slightly narrower and the peak temperature of β relaxation shifts higher. The β' relaxation is intensified markedly by irradiation.

Figure 3 shows the temperature dependence of mechanical loss in the range of 0–350°C for a non-irradiated specimen and specimens irradiated with 10 and 50 MGy. The mechanical loss of the β' relaxation increases and the peak temperature of the β relaxation tends to rise with increasing dose. The temperature of the onset of the sharp decrease in mechanical loss in the higher temperature region (>300°C) falls with increasing dose.

Figure 4 shows effects of thermal experience on the relaxation spectrum of specimens irradiated with 30 MGy by comparing the first and second runs. The γ relaxation peak is made narrower by irradiation, but broadens in the second run to the same width as that of a non-irradiated specimen. The mechanical loss in the β' relaxation decreases markedly in the second run, but is still higher in magnitude than in the second run for a non-irradiated specimen (*Figures 1* and *4*).

The shear modulus of the irradiated specimens are given as a function of temperature in *Figure 5*(a) for the first run and *Figure 5*(b) for the second run. At temperatures below the β relaxation, the shear modulus tends with increasing dose to increase in the first run, but to decrease in the second run. The decrement in shear modulus in the β relaxation region is scarcely affected by

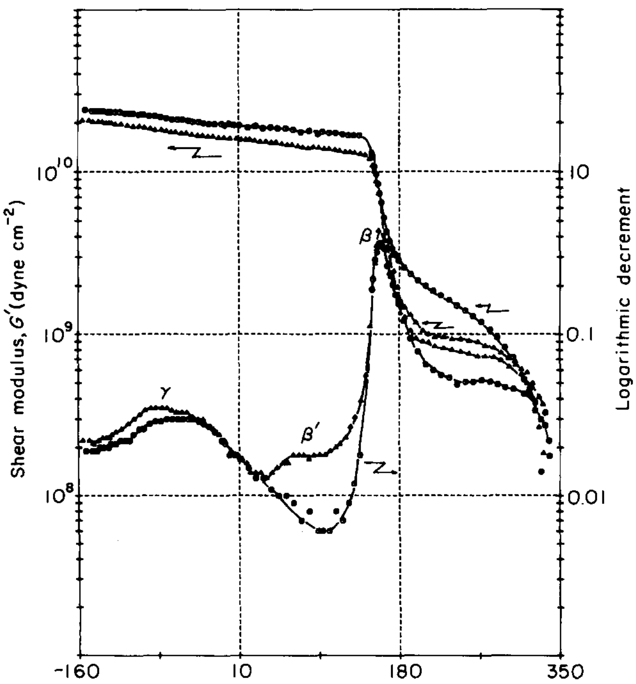

Figure 1 Mechanical relaxation spectra of semicrystalline PEEK. (▲) first run, (○) second run

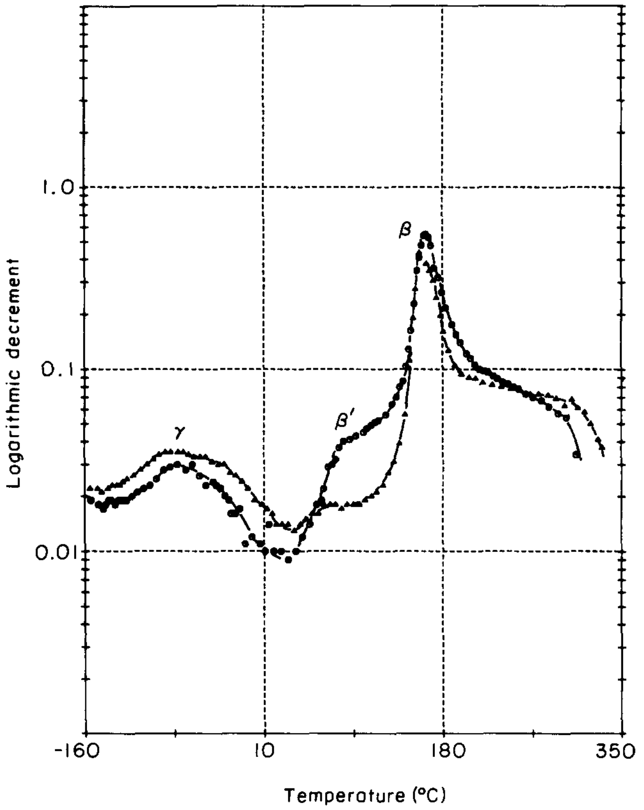

Figure 2 Effects of irradiation on mechanical loss. (▲) non-irradiated, (○) irradiated with 30 MGy

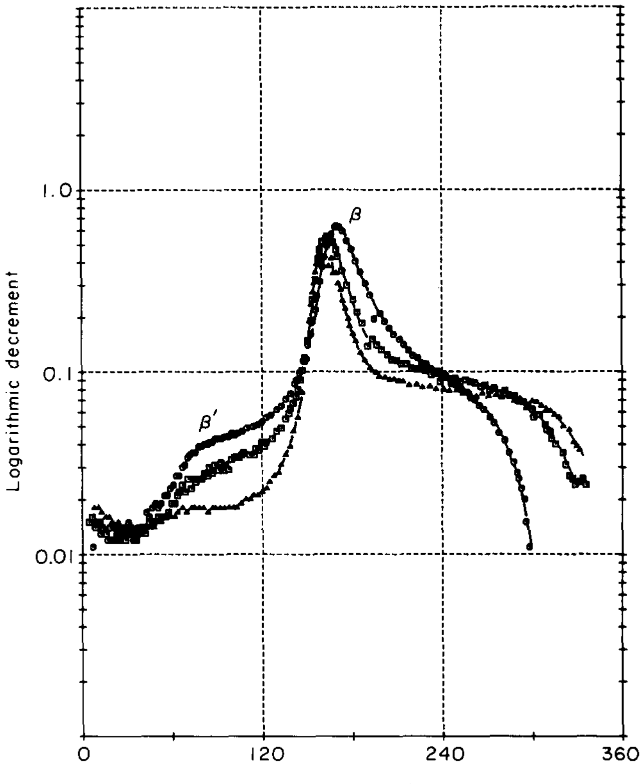

Figure 3 Mechanical loss *versus* temperature curves in β and β' relaxation regions. (▲) non-irradiated; irradiated with (☐) 10 MGy and (○) 50 MGy

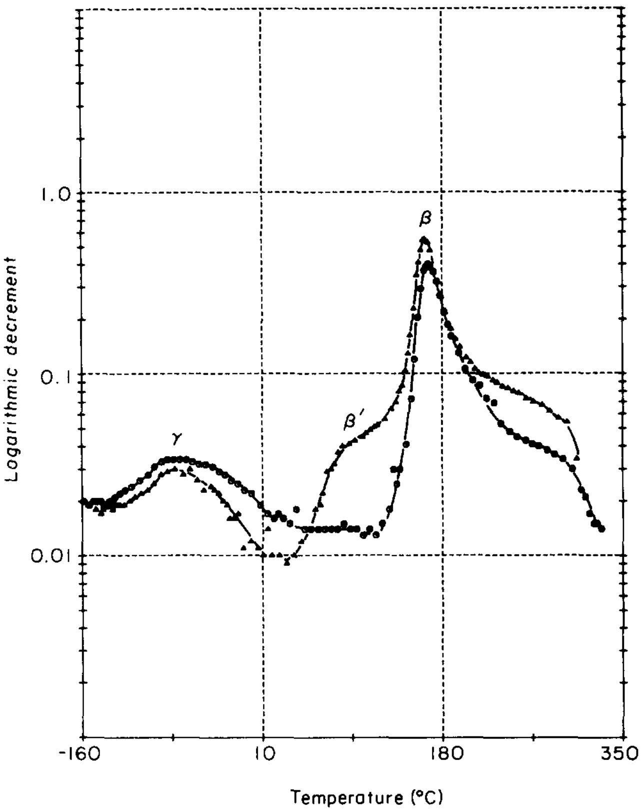

Figure 4 Comparison of mechanical loss between the first (▲) and second (○) runs for the specimen irradiated with 30 MGy

irradiation in the first run, but increases in the second run with increasing dose. The temperature of onset of fall in the shear modulus occurring in the higher temperature region (>300°C) falls with increasing dose.

DISCUSSION

Unirradiated PEEK

As shown in *Figure 1*, the β relaxation peak at 160°C is accompanied by a marked decrease in shear modulus, indicating that this relaxation is responsible for glassy to elastic transition. In general, a β relaxation is not observed distinctly in polymers of high crystallinity such as polyethylene. The existence of such a distinct β relaxation suggests that PEEK has non-crystalline region as a domain.

The profile of γ relaxation of semicrystalline PEEK is the same as that of non-crystalline PEEK in the 'dry' state reported previously[9]. The γ relaxation in rigid aromatic polymers such as poly(aryl ether), poly(arylsulphone) and poly(aryl ester) has been called a mechanical secondary relaxation or low temperature relaxation[10–12]. The γ relaxation of polymers such as polyethylene, poly(methyl methacrylate) and polystyrene has been attributed to molecular motions of short branching or local motion of chains existing on crystallite surface, or both. For rigid aromatic polymers, the low temperature mechanical relaxation has been attributed to local motion of aromatic units in the main chain[10–12]. The γ relaxation observed in the present study could be also assigned to the local motion of phenylene units in the main chain.

The mechanical loss in the range of −160°C to −40°C decreases in the second run. As reported previously[9], the γ relaxation peak of non-crystalline PEEK is affected by absorbed water; that is, the main peak at about −100°C in the 'wet' state shifts to −80°C and its magnitude becomes lower in the 'dry' state produced by vacuum drying. The small decrease in the mechanical loss in the range of −160°C to −40°C in the second run may be ascribed to further drying of the specimen by heating to over 300°C in the first run.

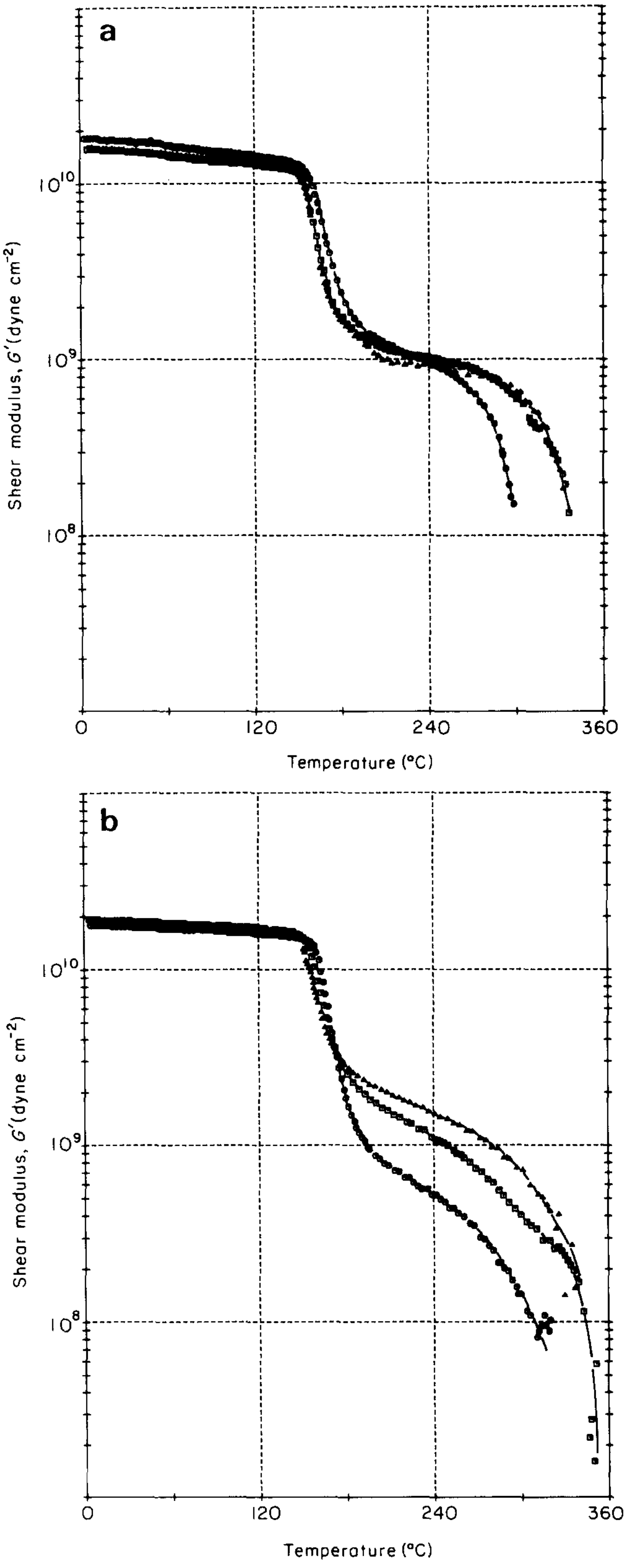

Figure 5 Temperature dependence of shear modulus in (a) first run, (b) second run for the specimens: (▲) non-irradiated; irradiated with (□) 10 MGy and (○) 50 MGy

As shown in *Figure 1*, the β' relaxation peak disappears in the second run. A similar relaxation was observed at just below the glass transition temperature for non-crystalline PEEK[9] prepared by rapid quenching from the molten state, and it was eliminated by heating up to the glass transition temperature. From the result of the thermal experiment the β' relaxation is considered to be due to molecular rearrangement from a quasistable state with a loosened chain packing introduced by rapid quenching to a more stable state consisting of rigid chain packing[9]. The absence of the β' relaxation in the second run shows that chain packing becomes more rigid during the first run.

Non-crystalline PEEK gives an α' relaxation peak at 180°C, corresponding to crystallization, but the α' relaxation is not found for the specimen with ~15% crystallinity. It has been reported for PEEK that the degree of crystallinity and the thickness of the actual crystalline region increase with crystallization temperature and that the attainable maximum crystallinity is as high as 45% or more[3,4]. As shown in *Figure 1*, the shear modulus increases in the second run. This shows an increased degree of crystallinity and indicates the occurrence of further crystallization during the thermal experience in the first run. However, the α' relaxation is absent in the first run for the specimen with 15% crystallinity. It could be considered that α' relaxation is responsible for formation of crystallites from the non-crystalline state but is not responsible for growth of crystallites.

Effects of irradiation on β' and β relaxation

As shown in *Figure 2*, irradiation results in the narrowing of the γ relaxation peak, the marked increase in mechanical loss in the β' relaxation region, and the shift of the β relaxation peak to higher temperatures.

In the measurement of the viscoelastic properties of non-crystalline PEEK, the α' relaxation peak that accompanies molecular rearrangement during crystallization was observed at 180°C; and it shifted to higher temperatures and its intensity decreased with increasing dose[9]. The changes in α' relaxation induced by irradiation are indicative of formation of a structure that inhibits crystallization. Along with the change in α' relaxation, the β relaxation peak was observed to shift to higher temperatures with increasing dose. It was concluded from the changes in α' and β relaxations induced by irradiation that a crosslinked structure is formed during irradiation. Although no information about the α' relaxation can be obtained in the present work where semicrystalline PEEK is used, the shift of the glass transition to higher temperatures also suggests the formation of crosslinked structure in non-crystalline region induced by high dose rate electron beam irradiation.

The intensity of the β' relaxation increases with increasing dose (*Figures 2* and *3*). This relaxation disappears in the second run (*Figure 4*). A similar relaxation has been observed in the same temperature range for irradiated polysulphones[13], poly(aryl ester) and non-crystalline PEEK[9]. As previously mentioned, the β' relaxation can be ascribed to the molecular rearrangement from loose chain packing to more rigid packing. When main chain scission takes place during irradiation, the chain ends introduced by scission should loosen the chain packing of the surrounding molecules. The observed enhancement of the β' relaxation in irradiated specimens indicates the increase in amount of loose chain packing. The decreased intensity of the β' relaxation in the second run shows that chain packing becomes more rigid during the first run. Enhancement of the β' relaxation by irradiation suggests that chain scission also occurs under high dose rate electron beam irradiation.

The mechanical loss in the β' relaxation region in the second run for the specimen irradiated with 30 MGy is still larger than that in the second run for the unirradiated specimen (cf. *Figures 1* and *4*) which shows that the chain packing in the irradiated specimen is still loose even after the first run by comparison with that for the non-irradiated specimen. Rearrangement from loose to rigid packing could be restricted by crosslinked structure.

Shear modulus decreases sharply at the glass transition. In the first run, the decrement in the shear modulus at the glass transition is affected little by irradiation (*Figure 5(a)*). Since the decrement in shear modulus at the glass transition corresponds to amount of non-crystalline chains, the results in *Figure 5(a)* indicate that degree of crystallinity is affected little by irradiation before any thermal experience is suffered. On the other hand, the decrement in shear modulus at the glass transition in the second run increases with dose (*Figure 5(b)*), which indicates that degree of crystallinity decreases after thermal experience at > 300°C in the first run. This shows that recrystallization from the molten state is inhibited by the crosslinked structure introduced during irradiation.

Radiation effects in the γ relaxation region

The details of the change in the γ relaxation induced by irradiation and thermal experience are shown in *Figure 6(a)* for the specimen irradiated with 30 MGy. The main γ peak of unirradiated PEEK exists at −80°C, and it has a shoulder in the range of −40°C to 0°C. This shoulder disappears and the peak profile becomes narrower under irradiation. The γ relaxation of PEEK may be complicated by overlapping of local motion of various phenylene units such as diphenyl ether, diphenyl ketone and their short repeating units. Disappearance of the shoulder seems to be the result of disintegration of some moiety among the above groups. However, it might be better to consider that the shoulder is related to a molecular motion of the moiety with an inherent conformation, because the shoulder appears again in the second run after suffering thermal experience over 300°C during the first run.

The marked decrease in shear modulus that corresponds to melting of crystallites is observed above 300°C and its temperature at onset falls with increasing dose (*Figure 5(a)*), which indicates that melting point decreases with increasing dose. The melting temperature is often discussed on the basis of crystallite size so that decrease in melting temperature indicates decrease in crystallite size[14]. Yoda reported recently radiation effects on X-ray diffraction of oriented semicrystalline PEEK[15]. The average crystallite size along the poymer chain direction is reduced by ~15% whereas the lattice distortion parameter and *c*-axis dimension of the unit cell are little affected on irradiation with 50 MGy. Decrease in crystallite size without change in distortion parameter and unit cell dimension possibly suggests that crystals are degraded in the vicinity of the crystalline–non-crystalline interface.

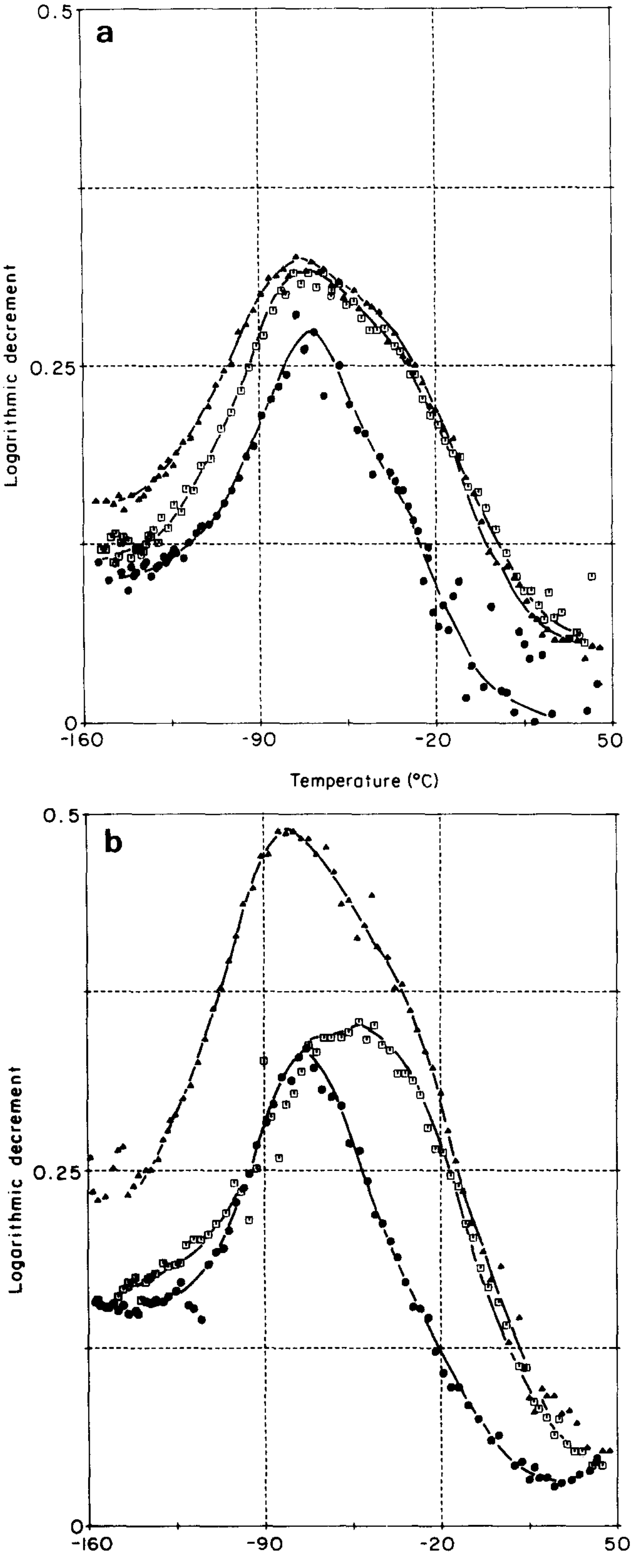

Figure 6 Detailed γ relaxation spectra for (a) semicrystalline, (b) non-crystalline PEEK. (▲) non-irradiated; irradiated with 30 MGy (●) first run, (□) second run

Radiation resistance of semicrystalline PEEK is slightly less than that of non-crystalline PEEK[5]. A similar phenomenon was reported for polyethylene, i.e. radiation resistance of polymer with high degree of crystallinity is lower than that with low degree of crystallinity[16]. As mentioned in the introduction, lower radiation resistance of crystalline polymers seems to be related to irradiation susceptibility of molecules with an inherent conformation.

On this basis, the following hypothesis is proposed. Disappearance of the shoulder on the γ relaxation peak induced by irradiation results from disintegration at specific sites, such as the crystalline–non-crystalline interface. Reapparance of the shoulder in the second run indicates that original chain conformation is reproducible during recrystallization in the first run. The shoulder might be assigned to the movement of chains existing at the interface between crystalline and non-crystalline phases (tie molecules).

Figure 6(b) shows the results of similar experiments carried out for non-crystalline PEEK. The same shoulder is observed in the non-irradiated specimen and it disappears with irradiation of 30 MGy as in the case of semicrystalline PEEK. Previously we have assumed that the molecular chains have partial alignment or orientation even in non-crystalline PEEK prepared by rapid quenching[9]. The fact that the shoulder on the γ relaxation peak behaves similarly on irradiation in both crystalline and non-crystalline PEEKs would support this assumption.

In the second run, the peak becomes binodal, with peaks at -80°C and -48°C. Since crystallization during the first run is severely hindered by crosslinked structure in irradiated non-crystalline PEEK, many imperfections may be formed in crystallites. The mode of molecular motion of the chains about the imperfection may be similar to that of chains existing at the crystalline–non-crystalline interface. It could be considered that a distinct peak recurs in the same temperature region as the shoulder because these two molecular processes overlap.

CONCLUSION

The discussion about the radiation effects on viscoelastic behaviour of semicrystalline PEEK leads to three conclusions. First, high temperature shift of the β relaxation peak and other facts indicate that PEEK undergoes crosslinking in a non-crystalline region. Appearance of the β' relaxation indicates that chain scission occurs at same time under high dose rate electron beam irradiation. Secondly, the disappearance of the shoulder on the γ relaxation peak induced by irradiation and reappearance of the shoulder after thermal experience during the first run suggests disintegration of chains existing in the vicinity of the crystalline–non-crystalline interface (tie molecules). Finally, lower radiation resistance of semicrystalline than non-crystalline PEEK is related closely to the disintegration of tie molecules between crystalline and non-crystalline phases.

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