Radiation effect of aromatic thermoplastic polyimide (new-TPI)

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Electron irradiation effects on tensile properties and molecular motion were studied for a newly developed thermoplastic aromatic polyimide (new-TPI). It has an extremely high glass transition temperature (250°C) and shows adequate tensile properties at high temperature. The strength and modulus measured at 23°C are scarcely affected by irradiation up to 100 MGy, but elongation after irradiation at 100 MGy decreases to 50% of the initial value. Strength and modulus at high temperature increased with irradiation. Information on changes in molecular motion revealed that the improvement in the high temperature properties is brought about by creation of crosslinking induced by non-oxidative electron irradiation.

(Keywords: aromatic thermoplastic polyimide (new-TPI); matrix resins for CFRP; electron irradiation; tensile properties; molecular kinetics)

INTRODUCTION

Aromatic polymers, the skeletons of which are composed of aromatic rings linked by various functional groups, are used for heat resistant materials and are expected to be used under severe conditions such as those in space. Recently, carbon fibre reinforced plastics (FRP) with aromatic polymer as matrix resin have been developed for high performance materials. It has been reported that carbon fibre reinforced poly-ether-ether-ketone (PEEK) and polyphenylenesulphone (PPS) have excellent interlaminar toughness and resistance to delamination compared with FRP with thermosetting matrix resin[1–3]. High performance fibre reinforced thermoplastics (FRTP) are expected to have applications in the structural materials of aeroplanes, artificial satellites and space stations.

To apply FRTP in the space environment, radiation stability is required. Aromatic polyimides, such as Kapton and Upilex, have good properties at high temperature and show excellent resistance to irradiation[4]. These polyimides are not, however, thermoplastic, so their use as a matrix resin for FRTP is impossible. FRTP with PEEK as matrix resin shows high radiation resistance[5], but FRTP that can be used at higher temperatures is required.

A new type of aromatic polyimide (new-TPI) has recently been developed by Mitsui Toatsu Chemicals Inc. New-TPI has a glass transition temperature of 250°C, which is 100°C higher than that of PEEK. The radiation resistance of new-TPI was studied by electron irradiation and the feasibility of application to FRTP is discussed from the viewpoint of thermal and radiation resistance.

EXPERIMENTAL

New thermoplastic polyimide

The new thermoplastic polyimide was supplied by Mitsui Toatsu Chemicals Inc. Its skeleton is composed of aromatic units and its glass transition temperature is 250°C. This polymer goes to the non-crystalline state on quenching and goes to the semi-crystalline state with heat treatment above the glass transition temperature. The crystallization rate is very small compared with that of PEEK.

Irradiation

Irradiation was carried out in air with a 2 MeV electron beam generated by a Dynamitron IEA-3000-25-2 electron accelerator installed in JAERI Takasaki. The dose rate was 5 $kGy\ s^{-1}$, which was measured with a cellulose triacetate (CTA) film dosimeter. To avoid the temperature of specimens rising during irradiation, all specimens were wrapped with aluminium foil (20 μm thick) and stuck on a water-cooled board with conducting adhesive. In this way the temperature of specimens was kept below 50°C during irradiation.

Tensile testing

Specimens for tensile testing were injection moulded. The shape of the specimen is shown in *Figure 1*. The crosshead speed was 5 $mm\ min^{-1}$ and temperatures were 23, 150, 200 and 240°C. Six specimens were tested under each condition.

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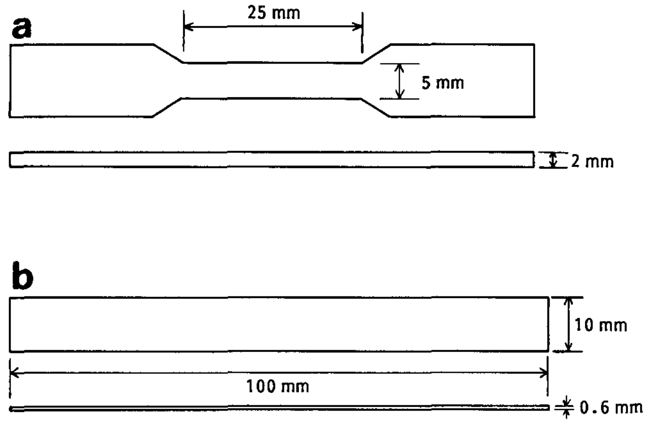

Figure 1 (a) Specimen for tensile test; (b) specimen for viscoelastic measurement

Dynamic viscoelastic measurement

The dynamic viscoelastic properties were measured in the range −150°C to 400°C by a torsion pendulum type apparatus (RHESCA RD 1100AD). Most specimens were annealed at 200°C for 1 h before irradiation and kept in vacuum until measurement.

RESULTS

Influence of irradiation on high temperature properties

Figure 2 shows the results of tensile tests measured at 23, 150, 200 and 240°C. Tests above 250°C could not be done because the tensile elongation is too large to be measured.

For unirradiated specimens, strength at break and Young's modulus decreased and ultimate elongation

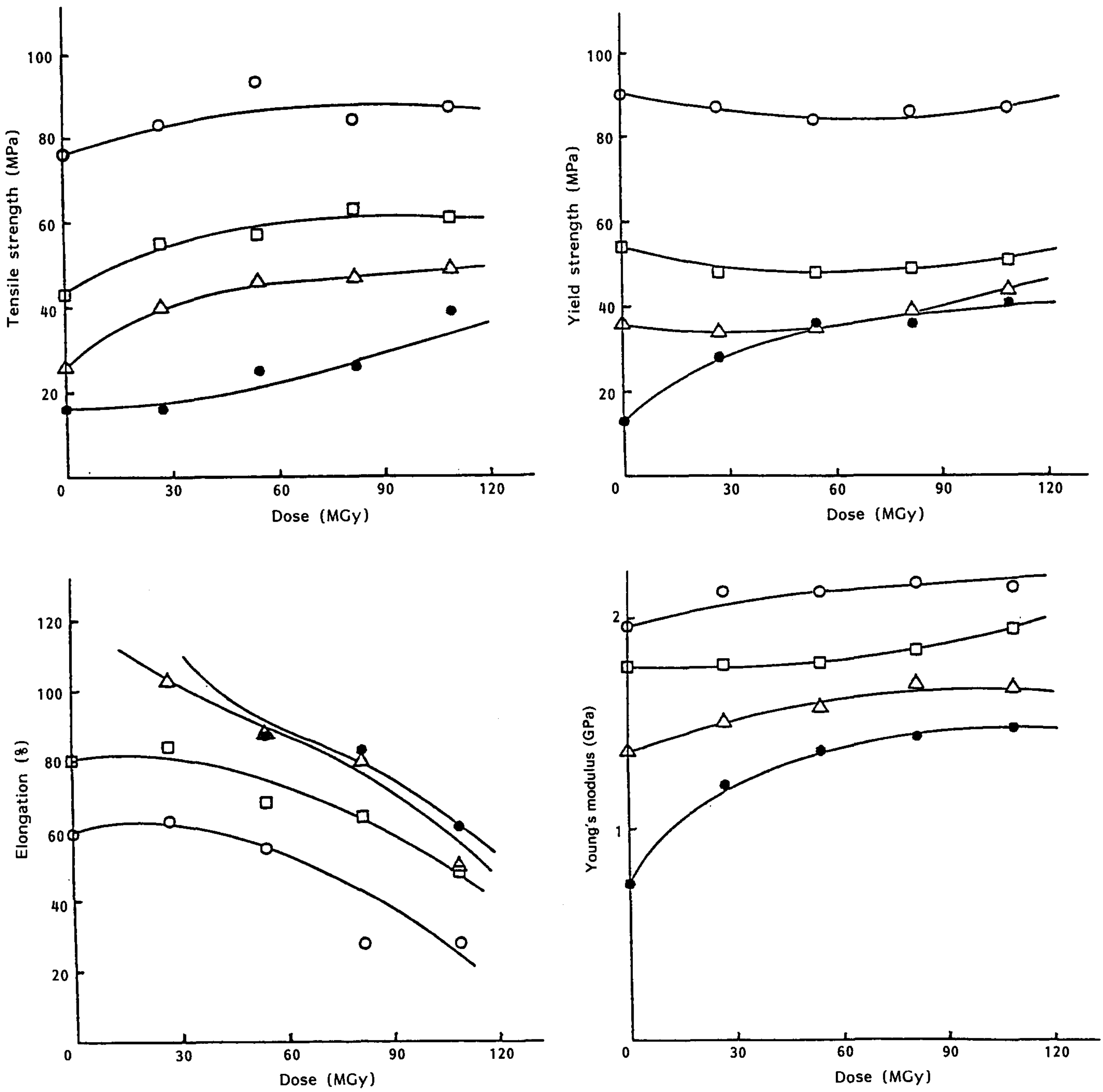

Figure 2 Tensile properties of electron irradiated new-TPI tested at: ○, 23°C; □, 150°C; △, 200°C; ●, 240°C

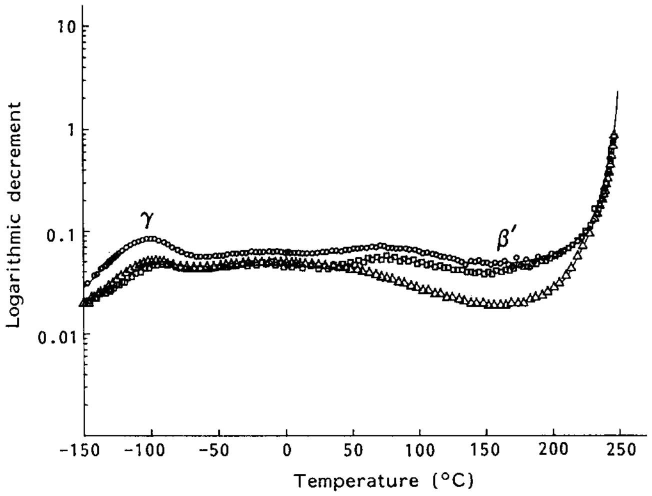

Figure 3 Mechanical loss *versus* temperature curves for new-TPI: ○, kept in normal humidity; □, dried with silica gel in vacuum; △, annealed at 200°C and kept in vacuum

increased with temperature. On irradiation, strength and Young's modulus tend to increase with increasing dose and tensile elongation tends to decrease. The changes induced by irradiation are more pronounced at higher temperature.

Changes in molecular kinetics

Figure 3 shows the temperature dependence of the logarithmic decrement of unirradiated specimens treated under three different conditions. One (wet) was kept in normal humidity, one (dry) was dried with silica gel in vacuum, and the other (dry) was annealed at 200°C and then kept in vacuum. These three specimens show a peak at about $-110°C$ (γ peak). In general, the γ relaxation of such a polymer having rigid chain configuration has been assigned to local motion of chains in the glassy state. The magnitude of the γ relaxation of the 'wet' specimen is larger than that of the 'dry' one.

The relaxation around 50–230°C observed in non-annealed specimens disappears on annealing. All specimens were annealed at 200°C before irradiation and measured in the 'dry' state, because it is then easier to determine the radiation effect.

Figure 4 shows the temperature dependence of the shear modulus and the logarithmic decrement of the unirradiated specimen. *Figure 4b* shows two peaks at 250 and 320°C, labelled β and α', respectively. There is a rapid decrease in shear modulus in the temperature range of the β peak. So the β peak should be responsible for conformational motion of main chains during glass transition. In the temperature range of the α' peak, shear modulus increases again, indicating that crystallization occurs. The α' peak is assigned to the rearrangement of chains in the crystallization process. The shear modulus then decreases again around $\approx 380°C$, indicating that newly formed crystallites melt at this temperature.

The mechanical relaxation spectra of irradiated specimens are shown in *Figure 5*. The magnitude of the mechanical loss below 50°C becomes smaller at higher dose. In contrast the magnitude in the temperature range 50–230°C (β' relaxation) increases with dose.

Figure 6 shows a comparison of the effects on the β' relaxation of quenching by immersion into water at room temperature from 260°C and irradiation. Circles show the mechanical loss of the specimen annealed at 260°C; squares represent the specimen quenched after annealing and triangles represent the specimen irradiated with 30 MGy after annealing. In the temperature range 100–230°C, the changes in logarithmic decrement of the quenched and irradiated specimens were almost the same.

Figure 7 shows the change in the logarithmic decrement due to irradiation in the temperature range 150–400°C. The peak of the β relaxation, i.e. the glass transition temperature T_g, shifts to higher temperature with dose. The change in peak temperature with dose is shown in

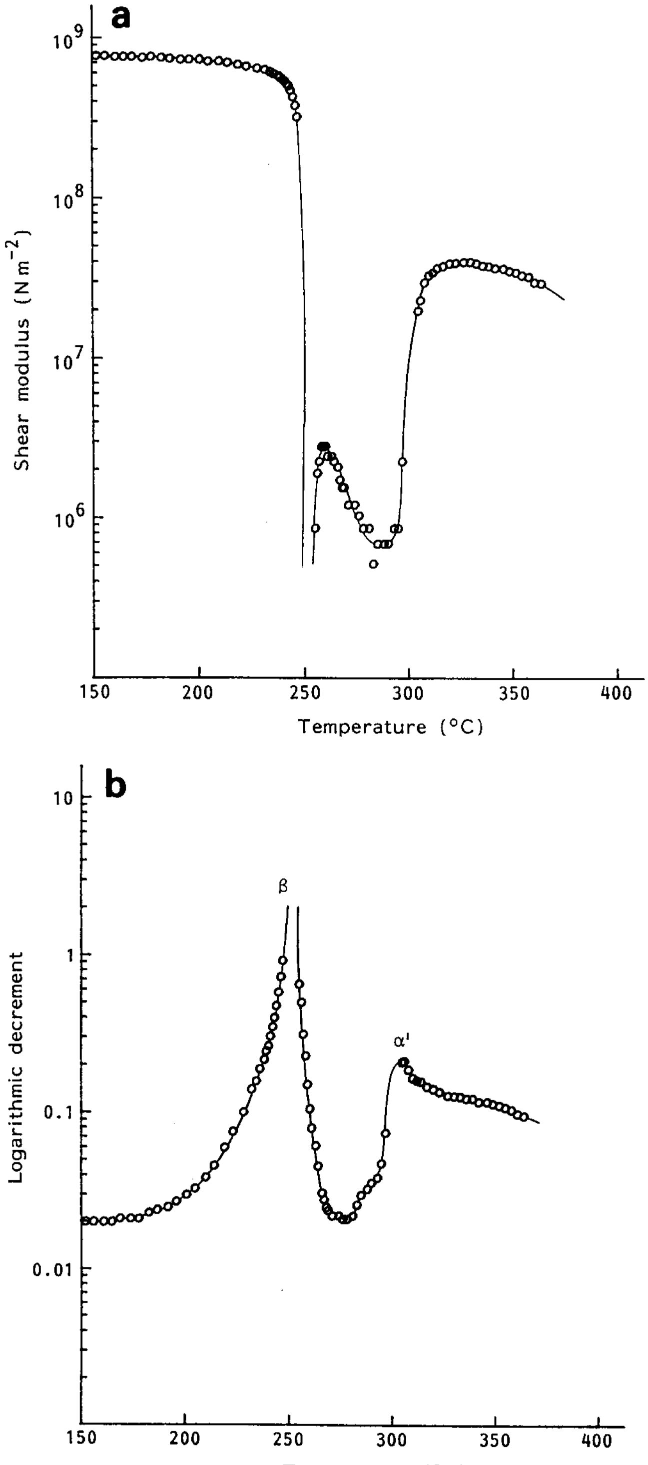

Figure 4 Mechanical spectra of new-TPI: (a) shear modulus; (b) mechanical loss

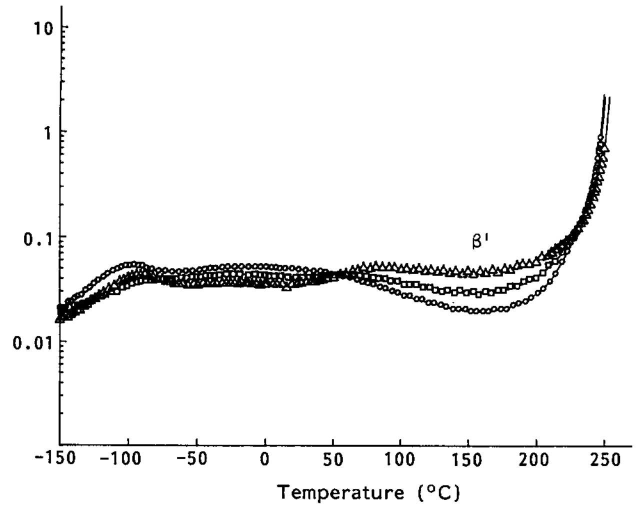

Figure 5 Effect of irradiation on mechanical loss: ○, not irradiated; □, 5 MGy; △, 30 MGy

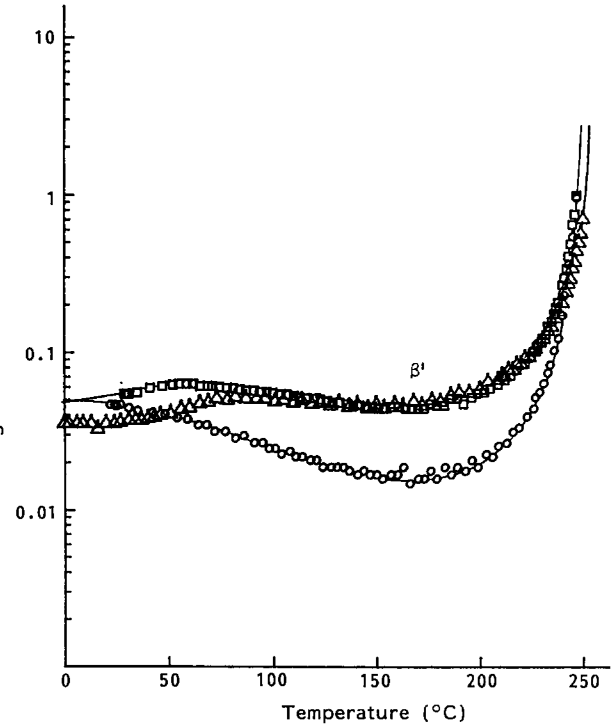

Figure 6 Comparison of effects of quenching and electron irradiation on mechanical loss: ○, annealed at 260°C; □, quenched from 260°C; △, irradiated with 30 MGy after annealing at 260°C

Figure 8. Circles show the peak temperatures of the specimens after irradiation; squares represent the specimens heat treated above 320°C after irradiation.

The α' peak in *Figure 7* shifts to higher temperature and its magnitude decreases with dose. The peak does not appear at 30 MGy. *Figure 9* shows the temperature dependence of the dynamic shear modulus in the α' peak region. The shear modulus decreases with dose up to 20 MGy and decreases rapidly near 400°C. For doses above 30 MGy, however, the shear modulus increases again and does not decrease even for temperatures $>$400°C.

Figure 10 shows the temperature dependence of the shear modulus for the specimens heat treated at 320°C after irradiation, at which the rate of crystallization becomes a maximum. The shear modulus of the unirradiated specimen shows a plateau after the glass transition and then abruptly decreases at 380°C. The profile of the specimen irradiated to 10 MGy is almost the same as that of the unirradiated specimen, but the temperature giving an abrupt decrease of modulus shifts to a lower value. With irradiation above 20 MGy, the shear modulus sharply decreases at the glass transition temperature similarly to the non-crystalline specimens and shows complicated behaviour.

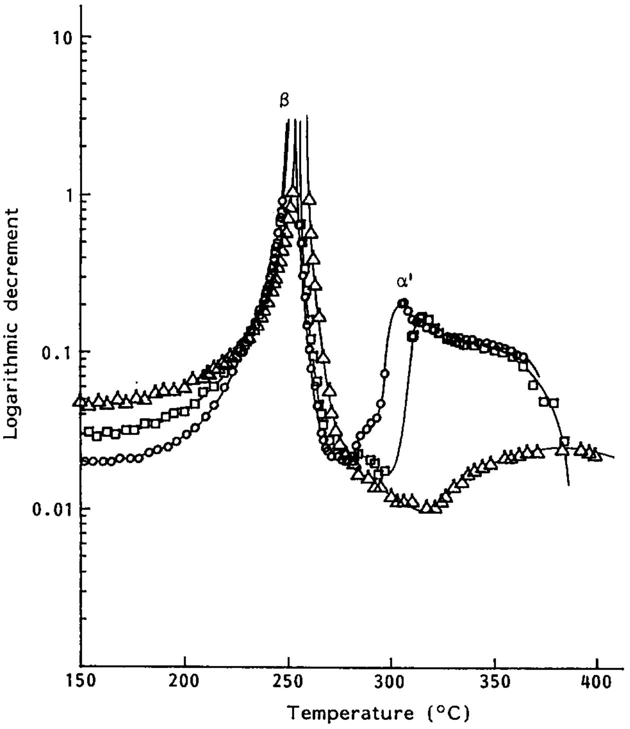

Figure 7 Effect of irradiation on mechanical loss: ○, not irradiated; □, 5 MGy; △, 30 MGy

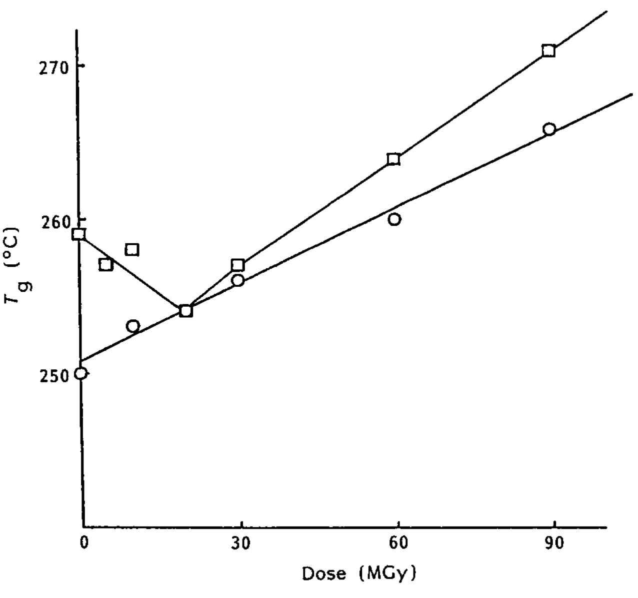

Figure 8 Change of glass transition temperature (peak temperature of β relaxation) with irradiation: ○, no heat treatment; □, heat treated above 320°C after irradiation

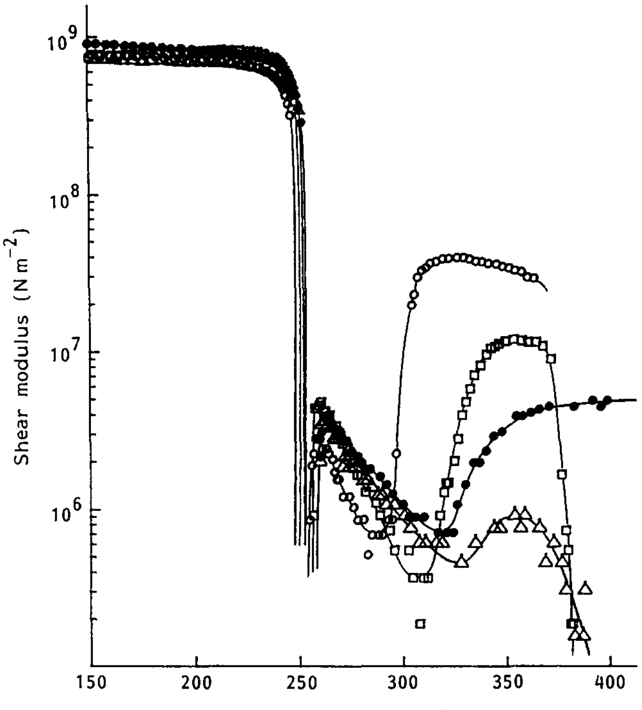

Figure 9 Temperature dependence of shear modulus: ○, not irradiated; □, 10 MGy; △, 20 MGy; ●, 30 MGy

DISCUSSION

γ, β and α′ peaks in logarithmic decrement

The γ, β and α′ peaks were assigned to a local motion of the chains in the glassy state, the conformational motion of main chains during glass transition and the re-arrangement of chains during crystallization, respectively.

The magnitude of the γ relaxation for the specimen in the 'wet' state is larger than that in the dry state. This phenomenon is observed for some polymers, such as aromatic polysulphone and PEEK. There are some reports about low temperature relaxation and that the relaxation is related to water molecules[6–8].

The α′ peak shifts to higher temperature and its magnitude decreases with dose. At the same time, the shear modulus becomes smaller with dose, indicating that irradiation causes the prevention of crystallization. The results in *Figure 10* also exhibit that degree of crystallinity and perfection of crystallite decrease with dose. These results indicate that irradiation introduces the cross-linking. The shift of glass transition towards higher temperature with dose (see *Figure 8*, circles) also indicates the formation of crosslinking.

As shown in *Figure 8*, the glass transition temperature of the specimens treated at temperatures above 320°C behaves differently *versus* dose. The shift of the glass transition to higher temperatures by heat treatment below 10 MGy can be interpreted in terms of generating friction of newly formed crystallites. On irradiation up to 20 MGy, the shift of the glass transition temperature decreases at once. This is due to decrease in the degree of crystallinity caused by radiation-induced crosslinking. It can be seen indeed that the degree of crystallinity decreases markedly at 20 MGy. The specimens heat treated after irradiation over 30 MGy have higher glass transition temperatures than the specimens which are not heat treated. The cause might be that crosslinking reaction is promoted by heat treatment above 320°C after irradiation.

Shear moduli above 320°C for the non-heat treated specimens decrease with dose up to 20 MGy (*Figure 9*). This also can be interpreted in terms of a decrease in degree of crystallinity. However, for the specimen over 30 MGy, the shear modulus above 320°C increases again. It could not be considered that the crystallization is promoted again, because the glass transition temperature increases above the higher dose region. Its magnitude is greater at higher dose. We currently have no explanation for this phenomenon and plan other measurements for clarification.

Radiation degradation and molecular structure

The modulus and strength of the unirradiated specimen decrease and the elongation at break increases with increasing testing temperature. In particular, at 240°C, just below the glass transition, modulus and strength decrease markedly and elongation is too large to be measured. On irradiation, modulus and strength at high temperature increase and elongation decreases to a measurable value even at 240°C, i.e. the high temperature properties are improved by irradiation.

The results of viscoelastic measurements clearly indicate that the crosslinking occurs and the glass transition shifts to higher temperature on irradiation. So we conclude that the improvement in high temperature properties results from the higher temperature shift of the glass transition and the creation of crosslinking structure.

β′ relaxation

The β′ relaxation almost disappears after annealing at 200°C, which means that the relaxation is related to the rearrangement of some local parts having quasi-stable chain packing[6]. The β′ relaxation appears again on

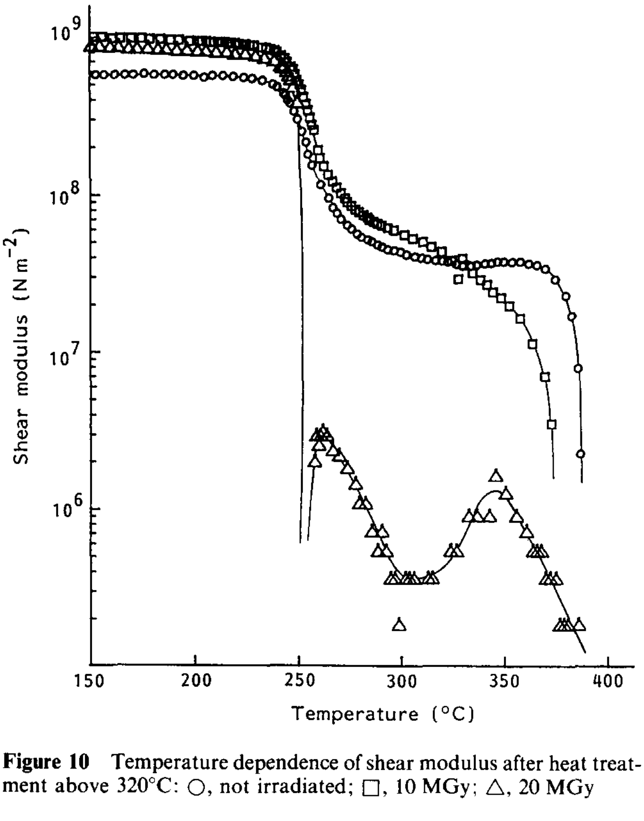

Figure 10 Temperature dependence of shear modulus after heat treatment above 320°C: ○, not irradiated; □, 10 MGy; △, 20 MGy

quenching from 260°C to room temperature and it occurs on irradiation too. The effects of quenching and irradiation give almost the same changes in the viscoelastic spectra, i.e. both quenching and irradiation make local parts which do not rearrange at room temperature[6]. The effect of quenching may be as follows. When the specimen in the state allowing three-dimensional movement is quenched, almost all chains become close packed but some small chains continue to exhibit quasi-stable chain packing. The effect of irradiation is difficult to imagine. There has been one explanation of how the β' relaxation appears after irradiation: the β' relaxation is related to chain ends which are induced with chain scission on irradiation[7]. Another explanation is now feasible. During irradiation, the energy is deposited in a small area and diffuses in a short time. Thus there is rapid quenching in a small area, i.e. specimens are quenched little by little during irradiation.

CONCLUSIONS

On electron beam irradiation, the elongation of new-TPI decreases to 50% of its initial value at 90 MGy, but strength and Young's modulus are stable up to 100 MGy. New-TPI has good performance at high temperature and irradiation improves properties at high temperature.

From information on the changes in molecular kinetics, the following three conclusions are drawn. First, by high dose rate electron irradiation the crystallization process is inhibited and, second, the glass transition is shifted to higher temperature. Third, these changes result from the formation of crosslinking.

We finally conclude that improvement in high temperature properties is due to crosslinking. New-TPI is a promising matrix material for thermal and radiation resistant FRTP.

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