Oxidative irradiation effects on several aromatic polyimides

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Radiation deterioration in mechanical properties under the oxidative condition (γ-rays under oxygen pressure) of polypyromellitimide (I), two copolymer type polyimides (II, III), two biphenyl tetracarboxylic acid anhydride type polyimides (IV, V) and polyetherimide (VI) was studied and was compared with the deterioration under the non-oxidative condition (high dose rate electron beam). Polyimides I–V showed a high resistance to radiation over 50 MGy under non-oxidative irradiation. Under oxidative irradiation they deteriorated at doses which were only 1/5 to 1/10 as strong as those used for non-oxidative irradiation. Measurements of the i.r. spectra and dielectric properties of polyimide I showed that the deterioration of mechanical properties under non-oxidative irradiation was mainly brought about by crosslinking. Under oxidative irradiation, mechanical properties were degraded by chain scission on imide and diphenyl ether moieties.

(Keywords: polyimide; oxidative irradiation; non-oxidative irradiation; tensile properties; dielectric properties; i.r. spectra)

INTRODUCTION

The polypyromellitimide Kapton has been used as a high performance thermo-resistant engineering plastic film. In recent years, several new aromatic polyimides having various chemical structures have been developed by various manufacturers and their performance is excellent. Because aromatic compounds are believed to be stable when exposed to high energy radiation, these polyimides are important materials which can be used in areas with a high radiation field, such as around fusion reactors and in space.

The effects of radiation on the polyimide Kapton have been well studied[1-7], but there are few studies of other aromatic polyimides[8-10]. We have studied the radiation effects on aromatic polymers having various chemical structures and reported that their radiation resistance depends on the chemical structures of repeating aromatic units[9,10].

Polymer materials are often used in environments affected by radiation-induced oxidative reactions, for instance environments where they are exposed to air with very low dose rate radiation over a long period. Therefore knowledge of radiation effects under oxidative conditions is important. We have studied radiation deterioration of mechanical properties under the conditions in which oxidation proceeds to the inside of material for six kinds of polyimides and compared the deterioration behaviours in the high dose rate electron beam irradiation. Further, differences in mechanisms of radiation-induced deterioration between the oxidative and the non-oxidative conditions were studied by means of measurements of infra-red spectra and dielectric properties for Kapton.

EXPERIMENTAL

Pyromellitimide type polyimide (I), two copolymer type polyimides (II, III), two biphenyl tetracarboxylic acid dianhydride type polyimides (IV, V) and polyetherimide (VI) were used as samples. These samples were supplied in a 50–125 μm thick film. The chemical structures of the repeating units are shown in *Figure 1*.

The specimens were irradiated in the shape of JIS No. 4 dumb-bell using an electron beam and ^{60}Co γ-rays. Electron beam irradiation was carried out under the same conditions reported previously (dose rate 5 kGy s^{-1} in air)[7]. Two irradiation conditions were employed for irradiation by γ-rays: a dose rate of 2.78 Gy s^{-1} in air, and a dose rate of 1.39 Gy s^{-1} under 0.7 MPa oxygen pressure. Irradiation was carried out at room temperature in all cases. As reported previously[11], the second irradiation condition was enough to allow radiation-induced oxidation to penetrate to the inside of 125 μm thick aromatic polyimide films.

The tensile tests were performed at 25°C with a cross-head speed of 200 mm min^{-1}. The Young's modulus was 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 was obtained from the stress at break point, and elongation was determined by simply dividing over-all displacement by the initial length of the dumb-bell neck (30 mm). These tensile parameters are represented by the average and standard deviation of five specimens.

The dielectric properties were measured in the frequency range of 30–1 $\times$ 10^5 Hz in the temperature range of -120 to 120°C using a bridge (TR-10C, Ando Electric Co. Ltd). The attenuated total reflection (ATR)

infra-red spectra were obtained by an *F T*i.r. spectrometer (JIR-100, Jeol Ltd).

RESULTS AND DISCUSSION

Deterioration behaviour

The changes in tensile parameters caused by irradiation under the three conditions are summarized in *Tables 1–6* for each of the polyimides. From the tables, the following changes are seen; with increasing dose, the tensile strength and elongation at break point decrease but Young's modulus tends to increase. Because the decrease in elongation is the most susceptible to irradiation among the changes in the tensile parameters, the degree of deterioration was evaluated based on the decrease in elongation.

The changes in elongation for polyimide I under various conditions are shown as a function of dose in *Figure 2*. Hereafter, the irradiation by electron beam will be termed 'non-oxidative irradiation' and irradiation by the γ-ray irradiation under oxygen pressure will be called 'oxidative irradiation'.

In oxidative irradiation, the elongation decreases sharply with dose, and when the irradiation is over 20 MGy elongation is nearly zero. The sharp decrease in elongation is probably brought about by chain scission caused by radiation-induced oxidation which penetrates to the inside of the material.

On the other hand, in non-oxidative irradiation, the elongation decreases exponentially with dose up to 30 MGy, but the decrease in elongation becomes less above 30 MGy (see *Table 1*). If the decrease in elongation is caused by only chain scission, elongation should reach to zero in the high dose region. It is presumed that the deterioration in the non-oxidative irradiation is caused by not only chain scission but by formation of crosslinking.

In the γ-ray irradiation in air, the elongation decreases in the same manner as in the non-oxidative condition in the initial stage and then decreases abruptly above 30 MGy. This abrupt decrease is probably caused by the penetration of the oxidized layer to the inside of material.

Tables 2 and *3* also show that the decrease in elongation with dose for polyimides II and III is vigorous in the
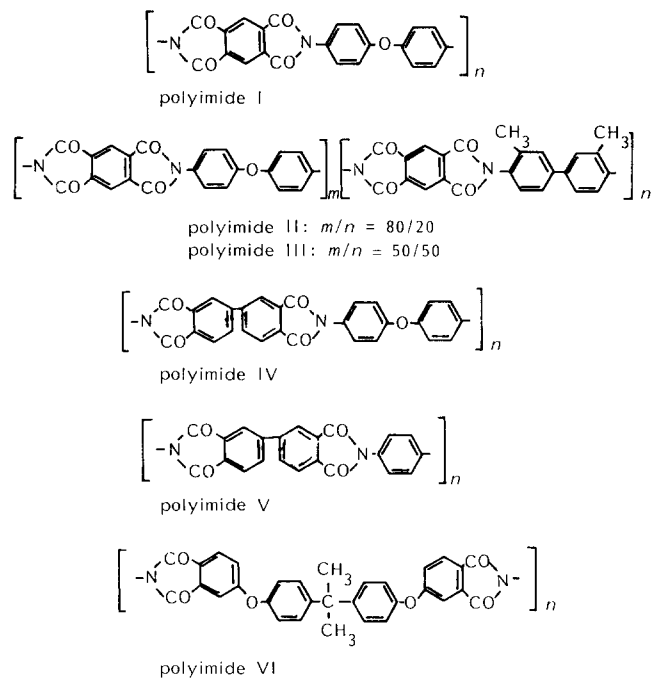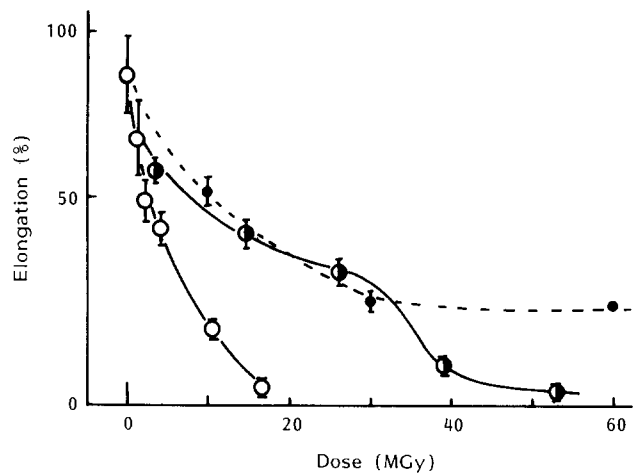

Figure 1 Chemical structures of the polyimides

Figure 2 Dose dependence of elongation for polyimide I: ●, electron beam; ◐, γ-rays in air; ○, γ-rays under 0.7 MPa oxygen pressure

Table 1 Tensile properties of polyimide I

Irradiation condition	Dose (MGy)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation (%)
Electron 5 kGy/s in air	0	1.83±0.07	224.2± 9.9	90±10
	10	1.93±0.04	192.9± 3.4	51± 3
	30	2.02±0.06	179.4± 3.9	25± 2
	60	2.02±0.06	186.7± 2.4	24± 1
	90	2.04±0.16	178.7±10.4	19± 3
	120	1.97±0.06	155.5±14.2	14± 4
Gamma rays 2.78 Gy/s in air	3.2	1.81±0.07	194.5± 6.1	56± 5
	14.6	1.91±0.02	177.0± 1.9	41± 3
	26.3	1.84±0.18	176.0± 3.4	32± 3
	39.1	2.28±0.06	126.1±10.2	9± 2
	53.0	2.26±0.22	70.8± 4.3	3± 1
Gamma rays 1.39 Gy/s under 0.7 MPa oxygen pressure	0.83	1.83±0.04	188.4± 5.0	63±10
	2.0	1.87±0.05	183.6±12.0	49± 5
	4.0	1.97±0.10	183.8± 8.9	42± 4
	10.2	1.91±0.17	148.4± 4.1	17± 2
	16.7	1.48±0.12	46.1± 5.1	3± 0.1

Table 2 Tensile properties of polyimide II ($m/n = 80/20$)

Irradiation condition	Dose (MGy)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation (%)
Electron 5 kGy/s in air	0	2.60±0.09	282.0±12.9	83±6
	10	2.69±0.20	265.2±12.6	63±3
	30	2.73±0.08	228.8±11.3	39±4
	60	2.79±0.11	244.4± 7.4	30±2
	90	2.83±0.12	203.8± 4.1	22±1
	120	2.76±0.15	119.1± 5.1	18±2
Gamma rays 1.39 MGy under 0.7 MPa oxygen pressure	4.1	2.47±0.05	188.1± 3.6	29±2
	9.3	2.62±0.10	171.1± 4.8	19±2
	16.8	2.66±0.06	154.5± 5.1	11±2

Table 3 Tensile properties of polyimide III ($m/n = 50/50$)

Irradiation condition	Dose (MGy)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation (%)
Electron 5 k Gy/s in air	0	4.81±0.15	354.5±19.0	33±8
	10	4.63±0.39	343.7± 6.7	33±5
	30	4.72±0.39	362.1±13.4	24±2
	60	4.96±0.46	300.1± 7.5	12±1
	90	4.94±0.26	282.2± 7.4	10±0.2
	120	4.94±0.62	273.0±23.8	8±1
Gamma rays 1.39 Gy/s under 0.7 MPa oxygen pressure	4.1	4.75±0.13	261.3± 2.9	11±1
	9.3	4.36±0.21	232.6± 5.9	6±0.5
	16.8	4.74±0.20	173.0± 8.0	4±0.3

Table 4 Tensile properties of polyimide IV

Irradiation condition	Dose (MGy)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation (%)
Electron 5 kGy/s in air	0	2.09±0.04	237.8±12.9	96± 7
	10	2.06±0.08	213.9± 6.2	81± 4
	30	2.19±0.06	198.2± 4.3	64± 3
	50	2.06±0.09	156.3± 3.3	26± 8
	60	2.05±0.12	156.7± 2.1	20± 2
	90	2.02±0.10	154.3± 1.7	14± 1
	120	2.08±0.16	148.0± 1.4	12± 2
Gamma rays 2.78 Gy/s in air	4.0	2.04±0.09	247.1±18.0	108±12
	9.6	2.14±0.04	255.5±14.9	114± 8
	20.1	2.05±0.14	207.7±11.9	87± 9
	33.6	2.17±0.10	176.8±10.5	66±11
	40.8	2.24±0.05	146.7± 2.0	32± 5
Gamma rays 1.39 Gy/s under 0.7 MPa oxygen pressure	2.1	1.92±0.14	223.1± 8.0	93± 5
	4.0	1.95±0.18	206.8±11.3	85±10
	10.3	2.15±0.14	193.9±11.7	81±12
	21.3	2.21±0.11	149.4± 5.9	38±19
	31.7	2.49±0.12	111.5±13.6	5± 1

Table 5 Tensile properties of polyimide V

Irradiation condition	Dose (MGy)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation (%)
Electron 5 kGy/s in air	0	5.16±0.15	399.6±17.2	50± 5
	10	5.14±0.30	395.8±22.4	37± 5
	20	5.25±0.28	390.9±14.4	35± 3
	30	5.36±0.09	373.2±11.5	30± 3
	60	5.48±0.13	357.2±11.7	24± 3
	90	4.47±0.25	342.4± 7.1	20± 2
	120	5.58±0.14	356.2± 7.0	21± 1
Gamma rays 1.39 Gy/s under 0.7 MPa oxygen pressure	4.9	5.14±0.60	341.2±16.8	26± 2
	10.9	5.22±0.25	296.8± 7.4	20±11
	19.6	5.88±0.30	212.2±21.7	5± 1

Table 6 Tensile properties of polyimide VI

Irradiation condition	Dose (MGy)	Young's modulus (GPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)
Electron 5 kGy/s	0	1.45±0.04	121.7±1.7	135.1±9.1	161±20
	3	1.58±0.10	116.0±4.3	103.0±4.9	42±20
	5	1.59±0.07	114.3±2.5	99.9±2.0	26±10
	7	1.64±0.10	116.1±3.5	97.2±3.0	25±21
	10	1.35±0.10	107.3±1.5	92.1±2.5	16± 5
	20	1.53±0.02	107.6±1.6		8± 1
Gamma rays 1.39 Gy/s under 0.7 MPa oxygen pressure	1.2	0.76±0.05		53.2±1.3	20± 9
	3.0	0.79±0.01		51.5±4.8	12± 3

oxidative condition but mild in the non-oxidative condition.

Polyimide I consisted of only 4,4'-oxydiphenylene pyromellitimide (A), but polyimides II and III are copolymers of the unit A and m,m'-dimethyl biphenyl pyromellitimide (B). It can be seen from the data on the three non-irradiated polyimides that the polymers which contain more B component in the chains exhibit larger tensile strength and smaller elongation, indicating that unit B is a 'harder' unit than unit A. The relation between the elongation and dose for polyimides I, II and III is summarized in *Figure 3*. In *Figure 3* elongation is represented by the normalized value of the initial elongation (residual elongation). The elongation of these three polyimides shows the same dose dependence under oxidative irradiation, but the dose dependence in the non-oxidative irradiation differs. The doses giving the half value of the initial elongation are 17, 25 and 43 MGy for polyimides I, II and III, respectively. This result suggests that the decrease in elongation with dose is less in the polyimide containing more of the 'hard unit'. It might be interpreted that 'hard unit' decreases the probability of crosslinking because it inhibits effective molecular motions in crosslinking.

Figure 4 shows the dose dependence of elongation for biphenyl-type polyimides IV. In this case also, the decrease in elongation with dose in the oxidative condition is remarkable compared with the non-oxidative condition, but the decrease in elongation with dose is less than that for polyimide I. This suggests that the biphenyl-type imide is more stable under radiation-induced oxidation than pyromellitimide. In the case of irradiation in air, elongation increases at first and then decreases rapidly. The same phenomenon was observed under irradiation by γ-rays in air for the poly(aryl ether-ether-ketone) PEEK[11]. This could be interpreted as resulting from a balance between scission on the surface and crosslinking in the inside of material. The sharp decrease in elongation in the high dose region is caused by enlargement of the oxidized layer over long periods of irradiation.

Figure 5 shows the dose dependence of the residual elongation for polyimides IV and V in the oxidative and the non-oxidative conditions. In the non-oxidative condition, the decrease in elongation for polyimide V is smaller than that for polyimide IV. This may result from differences in their probabilities to crosslink with each other. As seen from the molecular structures and the initial tensile properties, the mobility of the molecular
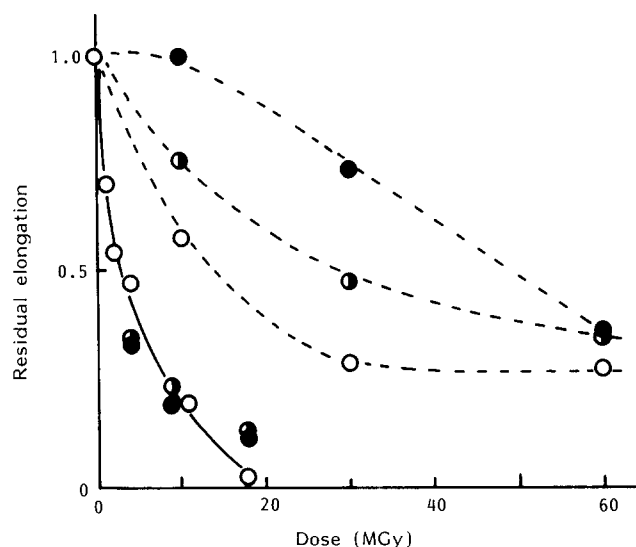

Figure 3 Comparison of radiation resistances for copolymer type polyimides; -----, non-oxidative condition; ———, oxidative condition; ○, (4,4'-oxydiphenylene pyromellitimide)/(m,m'-dimethyl biphenyl pyromellitimide) = 100/0; ◑, (4,4'-oxydiphenylene pyromellitimide)/(m,m'-dimethyl biphenyl pyromellitimide) = 80/20; ●, (4,4'-oxydiphenylene pyromellitimide)/(m,m'- dimethyl biphenyl pyromellitimide) = 50/50
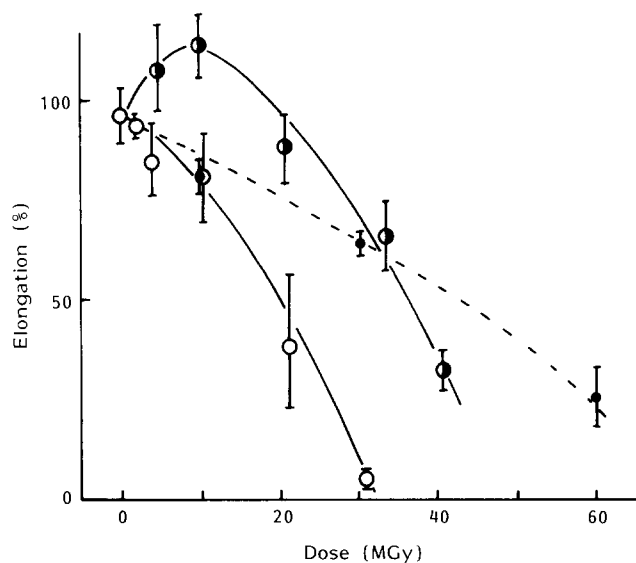

Figure 4 Dose dependence of elongation for polyimide IV: ●, electron beam; ◑, γ-rays in air; ○, γ-rays under 0.7 MPa oxygen pressure
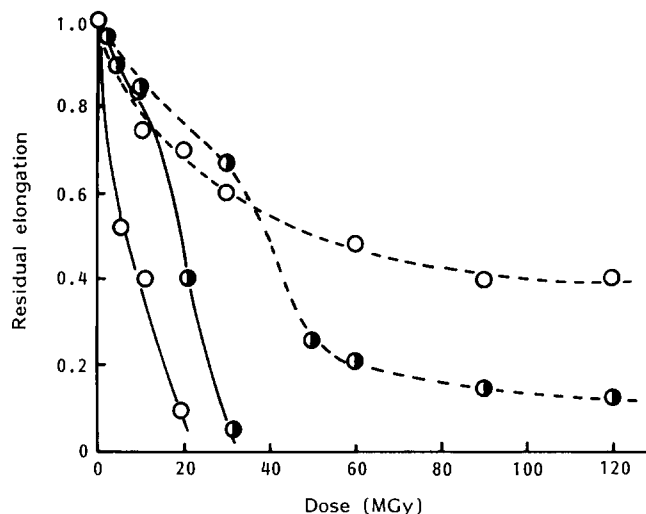
Figure 5 Comparison of radiation resistances between: ◑, polyimide IV; and ○, polyimide V; ———, the oxidative and -----, non-oxidative conditions

chains of polyimide V is presumed to be less than that of polyimide IV. In polyimide V, the probability of crosslinking would be reduced because the chains are less mobile.

On the other hand, the decrease in elongation in the oxidative condition for polyimide V is greater than for polyimide IV. The difference in the resistance under radiation-induced oxidation for both polyimides may be the result of differences in electronic states, but the details are not known.

Table 6 shows clearly that the radiation resistance of polyetherimide VI is considerably lower than the others. We have already reported that the aromatic polymers containing bis-phenol A unit in the main chain are susceptible to irradiation[9]. It is considered that the low radiation resistance of this polyimide is caused by damage in the bis-phenol A group.

In all polyimides the Young's modulus increases slightly with dose. For this reason we believe that inter- and/or intra-chain interaction is increased by accumulation of oxidation products during oxidative irradiation.

Deterioration mechanism

Judging from the deterioration behaviour it was presumed that crosslinking takes place mainly during non-oxidative irradiation and that chain scission occurs mainly during oxidative irradiation. To confirm this, microscopic damage was studied by measuring changes in infra-red spectra and dielectric properties of polyimide I caused by irradiation.

Infra-red spectroscopy

ATR infra-red spectra for the specimens irradiated under the non-oxidative and the oxidative conditions are shown in *Figure 6*. These spectra are produced by subtracting the absorbance for the unirradiated specimen from the absorbance for the irradiated specimen. This is based on the assumption that the absorbance of the skeleton vibration of aromatic rings is unchanged by irradiation. The upward peaks from the base line exhibit the components produced by irradiation. The downward

peaks demonstrate the components damaged by irradiation.

The changes in the infra-red spectra with dose for the specimens irradiated under the non-oxidative condition are less than those for the specimens irradiated under the oxidative condition. However, both show the following changes: (1) the absorbances responsible for carbonyl stretching in the imide ring (about $1700\,\text{cm}^{-1}$) and for nitrogen–aromatic ring stretching ($1376\,\text{cm}^{-1}$) decrease with dose; (2) the absorbance concerned with the asymmetric stretching mode of the diphenyl ether group ($1249\,\text{cm}^{-1}$) decreases with dose. These results show that imide and diphenyl ether moieties are both damaged under the irradiation conditions.

In the spectra for the specimen irradiated with 4 MGy under the oxidative condition, a pair of bands (1778 and $1739\,\text{cm}^{-1}$) and the band responsible for the carbonyl group ($1680\,\text{cm}^{-1}$) appear and their intensity increases with dose. The pair bands are well known characteristics of absorption of acid anhydride. As oxidation products increase, the damage in the imide and diphenyl ether moieties increases. It can be concluded that the decomposition of imide and diphenyl ether groups is promoted by the radiation-induced oxidation.

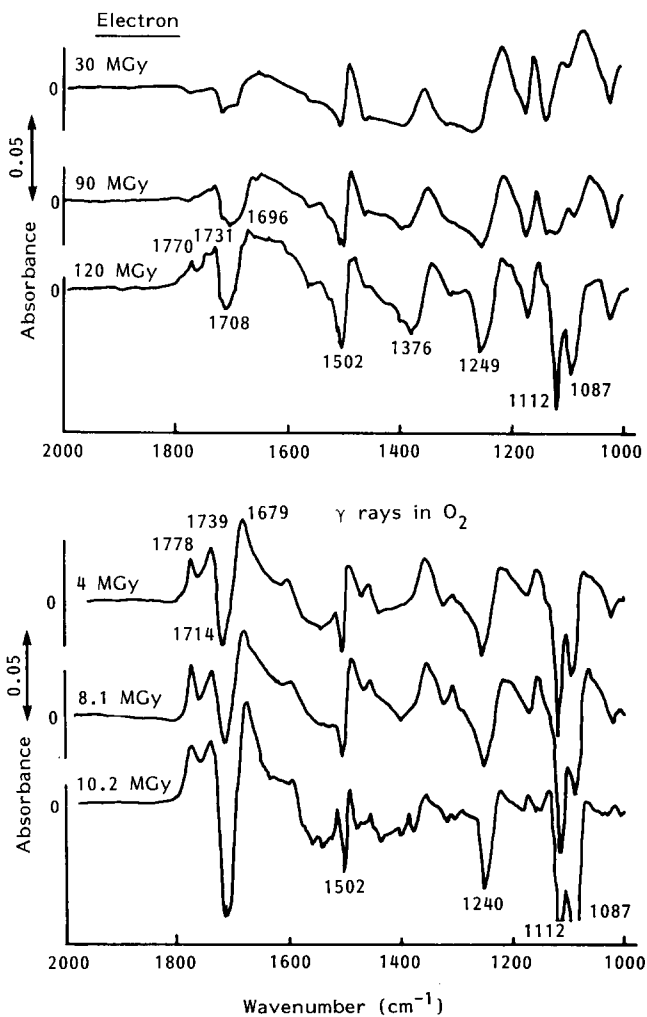In the spectra for the specimen irradiated by electron beam with 120 MGy, the pair band appears and intensity

Figure 6 ATR i.r. difference spectra of polyimide I irradiated under the non-oxidative and the oxidative conditions

at 1680 cm^{-1} increases also. This shows that the radiation-induced oxidation proceeds on the thin layer even during the irradiation by a high dose rate electron beam in air.

Dielectric properties

Figure 7 shows the temperature dependence of the dielectric loss factor of the non-irradiated specimens at various frequencies. It is well known in polypyromellitimide that a small number of water molecules absorbed in a material affect molecular motion at low temperature[12]. Therefore, dielectric measurements were performed on the specimens in conditions of normal humidity ('wet') and on specimens dried at 100°C for two hours in air ('dry'). Two relaxation regions are visible; the relaxation at the lower temperature region is observed as a peak (γ relaxation) and the one at the higher temperature region is observed as a shoulder (β relaxation).

The loss maximum of the γ relaxation in the wet state measured at 10 kHz exists at $-30°C$ and the activation energy calculated from the shift of peak temperature on frequency is 9.9 kcal mol^{-1}. Bernier and Kline reported that the mechanical γ relaxation peak of polypyromellitimide was observed at $-43°C$ (9.3 kHz) and the activation energy was 11.4 kcal mol^{-1} (ref. 13). They explained the γ relaxation as a local motion of the main

chain enhanced by the water molecules attached and held to carbonyl atoms by hydrogen bonds. The γ relaxation we observed would have the same mechanism.

The magnitude of loss in the γ relaxation region is reduced by drying and the peak is shifted to higher temperature. This should be caused by desorption of water molecules. Butta *et al.*[12] reported that the mechanical γ relaxation vanished after drying at 200°C in vacuum. As seen in *Figure 7*, the small relaxation peaks are observed in even the dry state. This may result from traces of water which remain after drying at 100°C for 2 h.

The dielectric loss in the β relaxation region tends to increase with increase in temperature. In contrast to the γ relaxation, the magnitude and the dispersion profile are scarcely affected by drying. This relaxation is thought to be due to a torsional oscillation of aromatic rings[12], but exact assignment has not been carried out.

The dielectric dispersion curves in the dry specimen irradiated by electrons at 120 MGy and of the specimen irradiated under the oxidative condition at 21.1 MGy are shown in *Figures 8a* and *b*, respectively. The γ relaxation peaks are shifted to higher temperatures. Even though the γ relaxation is responsible for the local motion of the main chain enhanced by traces of absorbed water molecules, the shift of the peak temperature should reflect the change in the mode of the local motion caused by damage in the imide and/or diphenyl ether moieties.

A marked change by irradiation appears in the β relaxation region, i.e. the dielectric loss increases sharply
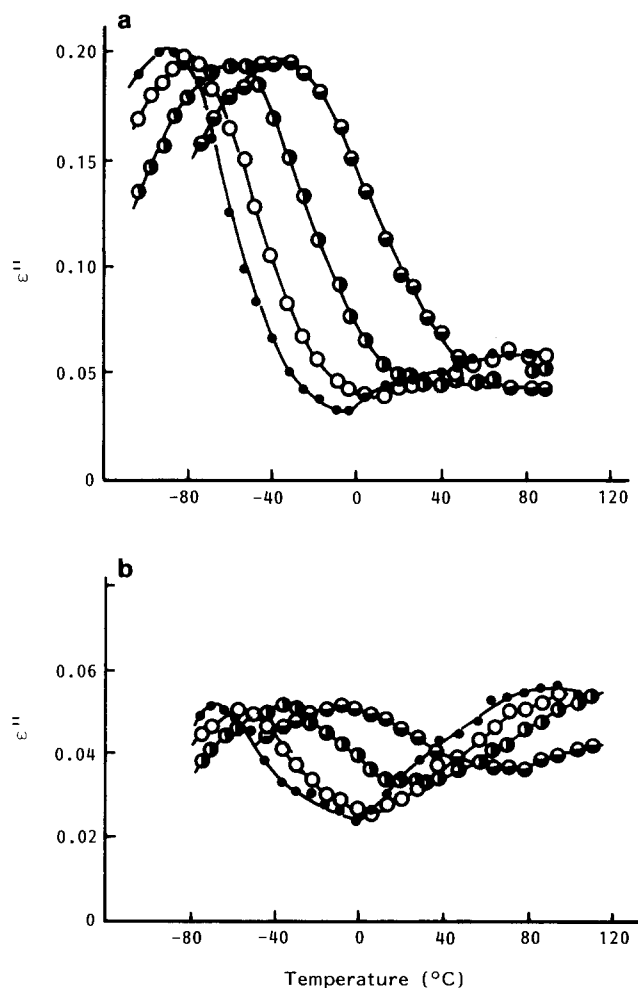

Figure 7 Dielectric dispersion curves for the non-irradiated polyimide I in: (a) 'wet' state and (b) 'dry' state. ●, 30 Hz; ○, 110 Hz; ◐, 1 kHz; ◓, 10 kHz
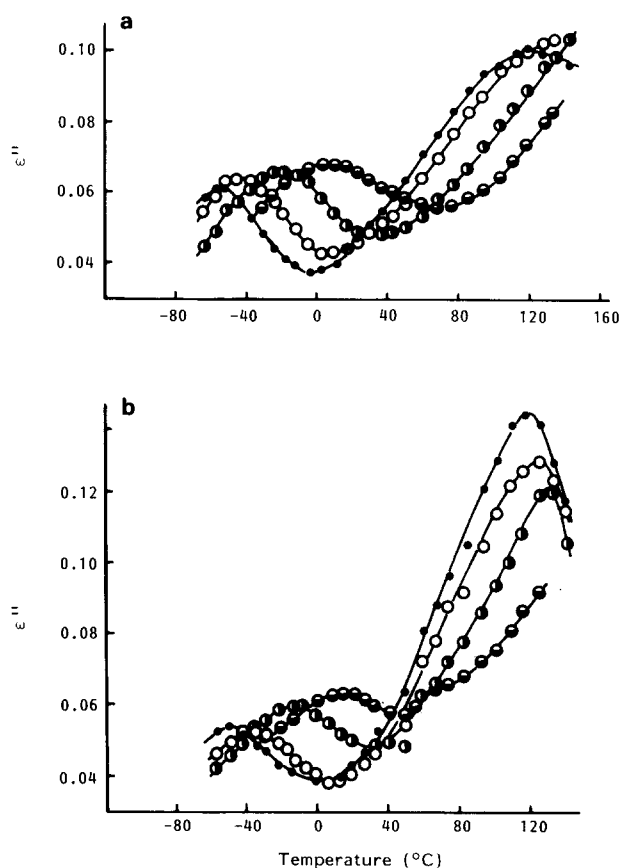
Figure 8 Dielectric dispersion curves in 'dry' state for the polyimide I irradiated under the non-oxidative condition: (a) with 120 MGy and (b) the oxidative condition with 21 MGy. ○, 30 Hz; ●, 110 Hz; ◐, 1 kHz; ◓, 10 kHz
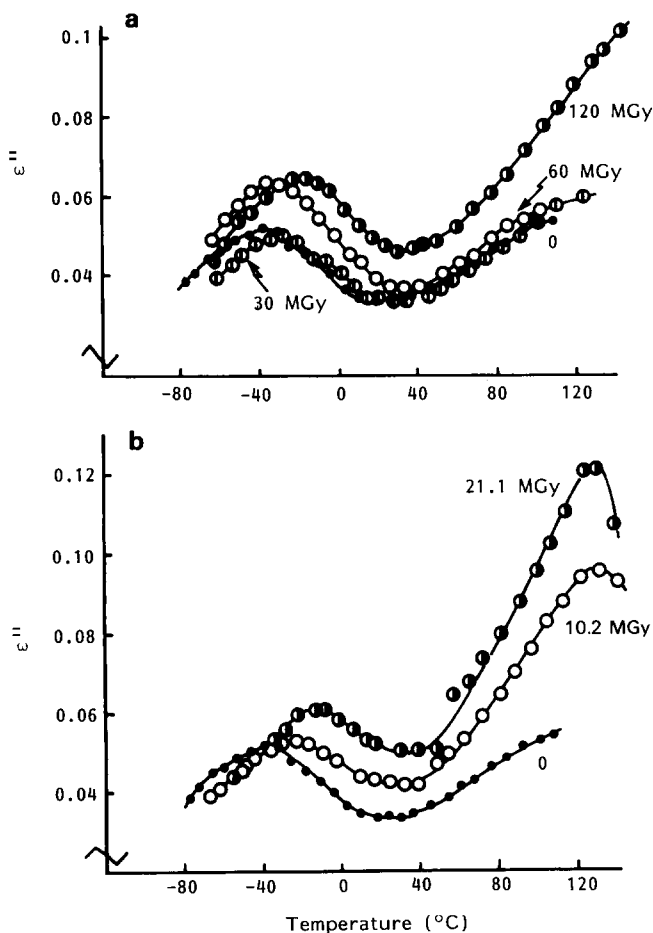
Temperature (°C)

Figure 9 Dielectric dispersion curves measured at 1 kHz in the 'dry' state for the specimens irradiated under the (a) non-oxidative and (b) oxidative conditions with various doses

with temperature and then a peak is formed. A divergent increase in the dielectric loss above room temperature was observed in poly(pyromellitamic acid) and polytrimellitamideimide which have amide–acid structures[14]. The results in the infra-red spectroscopy show clearly that decomposition of imide moiety proceeds during the oxidative irradiation. It may be that the sharp increase in the dielectric loss in the β relaxation region is closely associated with the motion of the amide–acid structure caused by decomposition of the imide ring.

Figures 9a and *b* show the changes in dielectric dispersions measured at 1 kHz for the specimens irradiated with various doses under non-oxidative and oxidative conditions, respectively. Under non-oxidative irradiation, the relaxation behaviour in the γ and β regions is scarcely affected up to 60 MGy, while in the specimen irradiated with 120 MGy, the behaviour in both regions is considerably affected. It can be concluded for the microscopic damage in the non-oxidative irradiation that decomposition of imide ring and diphenyl ether moieties are less up to 60 MGy, but increase in the higher dose region.

In contrast to the non-oxidative irradiation, clear changes in the relaxation behaviour are observed in the specimen irradiated with 10.2 MGy. This shows that decomposition of imide and diphenyl ether moieties occurs within the low dose region in the oxidative irradiation.

CONCLUSIONS

The information from infra-red spectroscopy and the measurement of dielectric properties indicates that the imide and diphenyl ether moieties are subjected to marked damage by irradiation under oxidative conditions. It can be concluded that vigorous deterioration of the mechanical properties under oxidative irradiation is caused by chain scission. On the other hand, although there is no marked damage in chemical structures caused by non-oxidative irradiation up to 60 MGy, a large decrease in elongation is observed as seen in *Figure 2*. Crosslinking plays an important role in the deterioration of mechanical properties under non-oxidative irradiation, because the decrease in elongation is brought about by not only chain scission but by crosslinking. The results in the copolymer type polyimides shown in *Figure 3* support this idea.

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