J. Inst. Electrostat. Jpn.

静電気学会誌, 24, 3 (2000) 146-152

論　文

Positron Lifetime and TSC of Electron Beam-Irradiated PEEK

Katsuyoshi SHINYAMA* and Shigetaka FUJITA*

(Received October 8, 1999; Accepted March 27, 2000)

In this study, polyetheretherketone (PEEK) was irradiated with an electron beam at a high dose; the longest-living component of the positron lifetime (τ_3) and the thermally-stimulated current (TSC) were measured to examine the internal structural changes in the irradiated specimens and the influence of the structural change on electrical properties. Measurements of τ_3 showed that τ_3 decreased by electron beam irradiation in a temperature range beyond the glass transition temperature (T_g) and that the free volume shrank. Measurements of TSC showed that the TSC peak temperature of the irradiated specimens shifted to a higher temperature and the peak temperature difference between irradiated and non-irradiated specimens grew for a higher poling temperature (T_p) regardless of the poling voltage (V_p). At T_p = 140°C, the TSC peak value tended to gradually decrease with an increase in the irradiation dose. At T_p = 180°C, however, the peak value was larger at 50 MGy compared to the non-irradiated specimens and it also decreased with an increase in the irradiated dose above 50 MGy. These results indicated that the number of dipoles and ions increases with increases in the exposure dose from the electron beam, but for doses over 50 MGy the crosslinking effect is clearly present, so the free volume shrinks and thus impedes polarization.

1. Introduction

High-polymer insulating substances are used in nuclear reactors and radiation facilities as materials for parts in electrical equipment. Outer space and nuclear fusion reactors are extremely severe environments involving high or very low temperatures and large vacuums in addition to high-energy radiation. Therefore, the challenge is to develop and apply a new high-polymer insulating material that can withstand such severe conditions.

Polyetheretherketone (PEEK) is considered to have excellent resistance to heat and radiation among special engineering plastics and is attracting attention as a next-generation electrical insulating material.[1] However, there are many unknowns regarding PEEK's electrical properties when subject to radiation, and these factors must be clarified quickly. Thus, polyetheretherketone (PEEK) was irradiated with electron beams in high doses and the internal structural changes of the irradiated specimens and the influence of such changes on the electrical properties were investigated. In this study, variations in the free volume due to electron beam irradiation were examined using a positron annihilation method, followed by measurement of thermally stimulated current (TSC) for various poling voltages (V_p) and poling temperatures (T_p). Then, the total charge (Q_{TSC}) and activation energy (H) were derived from TSC spectra. Changes in the polarization process due to electron beam irradiation were investigated.

2. Specimens and experiment method

2.1 Specimens

A PEEK film, TALPA-2000 made by Mitsui Toatsu, Chemicals Inc., was used as the specimen. Figure 1 shows the chemical structural formula of PEEK. Electron beam radiation of the specimen was performed in air using the electron accelerator from the Takasaki Research Center at the Japan Nuclear Power Research Institute. The acceleration voltage was 2 MV, the energy level of the irradiated electron beam was 1.95 MeV, and the dose rate was 10 kGy/s. Three values of

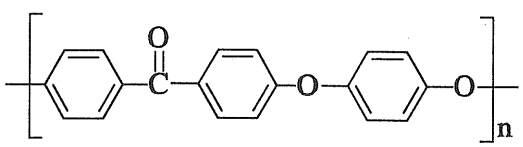

Fig. 1. Chemical structural formula of PEEK.

Keywords: Polyetheretherketone, Thermally-stimulated current, Positron Annihilation, Electron beam irradiation

*Department of Electrical and Electronic Engineering, Hachinohe Institute of Technology, 88-1, Myo Ohbiraki, Hachinohe 031-8501, Japan
E-mail correspondence to: Shinyama@hi-tech.ac.jp

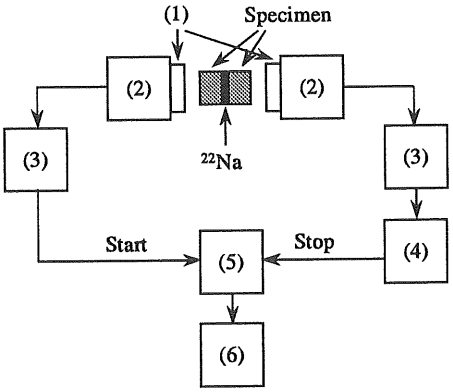

Fig. 2. Block diagram for the positron lifetime measuring equipment.

(1) Plastic Scintillation Detector, (2) Photo multiplier, (3) Differential Constant Fraction, (4) Delay Line, (5) Time-to-Voltage Converter, and (6) Pulse Height Analyzer.

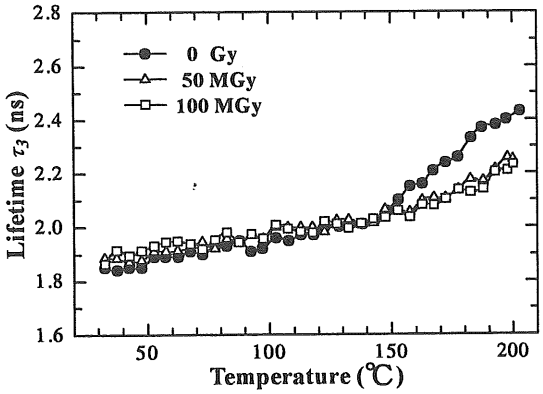

Fig. 3. Temperature dependence of τ_3.

Table 1 Average sizes of free volume

Dose (MGy)	V_{AVE} (nm^3)	
	143℃	183℃
0	0.099	0.130
50	0.099	0.114
100	0.100	0.110

irradiation doses used were 50, 75, and 100 MGy.

2.2 Experiment method

Figure 2 shows a block diagram of the positron lifetime measuring equipment. The positron lifetime was measured with ^{22}Na, the radiation source, inserted between two PEEK sheets with an individual thickness of 1 mm, and this assembly was set between scintillators. Because ^{22}Na emits a 1.28-MeV gamma ray when it emits a positron, this gamma ray was used as the starting signal for this equipment. Upon annihilation of a positron, two photons and a 0.51-MeV gamma ray are simultaneously emitted. This gamma ray was used as the stopping signal. The time difference between these gamma rays was measured by a time-to-voltage converter to determine the lifetime of positrons. At a heating rate of 5°C/h, the temperature was raised from 20 to 200°C when the long-life positron component (τ_3) was measured.

The thermally-stimulated current (TSC) was measured using a 50 μm-thick PEEK film that was irradiated with electron beams, followed by deposition of aluminum at the center on both sides to form electrodes with a diameter of 25 mm. Then, a short circuit was formed between the electrodes as the specimens were subjected to heat treatment by heating them from 30 to 220°C at a heating rate of 1°C /min in dry air. This heat treatment was performed to reduce the influence of trapped electrons brought about by irradiation. The spontaneous current was measured simultaneously at that time, and the direction of the current was positive. The poling temperature (T_p) was set at 140°C, which is close to the glass transition temperature (T_g = 143°C) of the non-irradiated PEEK; at 100°C, which is lower than T_g; and at 180°C, which is higher than T_g. The prescribed poling voltages (V_p = 0.5, 1.0, and 1.5 kV) were applied for a poling time (t_p) of 1 hr, followed by rapid cooling of the specimens and electrode system with the voltages applied. Then, a short circuit was formed between the electrodes again; the specimens were heated under the same environment and at the same heating rate as the heat treatment process. A vibrating reed digital electrometer (ADVANTEST, TR8411) was used to measure TSC.

3. Results and discussion

3.1 Longest-living component of the positron lifetime

Figure 3 shows the temperature dependence of the longest-lived component of the positron lifetime (τ_3). With the non-irradiated specimen, τ_3 gradually lengthened with increasing temperature and began to rapidly increase from 145°C. The variation of τ_3 corresponded to the variation of the free volume,[2] and the temperature at which τ_3 increased rapidly almost agreed with the glass transition temperature (T_g) of non-irradiated PEEK. This implies that the molecular Brownian movement grew active and the free volume became larger. With the specimens irradiated to 50 and 100 MGy, the same tendency as with the non-irradiated specimen was seen below 145°C. At higher temperatures, however, the rate of increase for τ_3 shrank, which may have been caused as a result of electron beam irradiation producing crosslinking among molecules; the increase in free volume was suppressed above T_g. Assuming that the free volume is a well potential (radius

R) of infinite depth, Equation (1) will hold for τ_3 and R[3)]

$$\tau_3 = \frac{1}{2}\left\{1 - \frac{R}{R+dR} + \frac{1}{2\pi}\sin\left(2\pi\frac{R}{R+dR}\right)\right\}^{-1} \quad (1)$$

where, dR is the extent of the electron layer and takes a value of 0.166 nm for solids. R can be found from Equation (1), and the average free volume, V_{AVE}, can be evaluated from Equation (2):

$$V_{AVE} = \frac{4}{3}\pi R^3 \quad (2)$$

Table 1 shows V_{AVE} derived from the above formula for specimens. If the specimen temperature is 143°C, which is the T_g of non-irradiated specimens, V_{AVE} will be 0.099 to 0.100 nm^3 for any specimen, with very little difference between doses. At 183°C, which a further 40°C higher, however, V_{AVE} was 0.130 nm^3 for non-irradiated specimens while it was 0.114 nm^3 at 50 MGy and 0.110 nm^3 at 100 MGy. That is, V_{AVE} decreased due to electron beam irradiation. In this way, the free volume was evaluated for each specimen. Results indicate that irradiation by electron beams causes the effects of crosslinking to be manifested above T_g.

3.2 TSC of non-irradiated and 100-MGy irradiated specimens

Figure 4 shows the results of TSC measurement of non-irradiated (0 Gy) specimens. At T_p = 100°C, the TSC peaked very faintly for V_p = 0.5 kV. For a larger V_p, however, a peak around 10 pA was observed near 120°C. At temperatures above 180°C, spontaneous current rapidly flowed and no peak was observed. At T_p = 140°C, TSC peaked near 157°C regardless of the value of V_p. The peak value increased with an increase in the V_p value. At T_p = 180°C, the TSC increased gradually from near 130°C and peaked near 170°C regardless of V_p. The peak value was 150 pA or over. Since the TSC peak appeared at a temperature slightly higher than T_p at T_p = 100°C and T_p = 140°C, this result is thought to be due to ionic space-charge polarization. The TSC peak at T_p = 180°C appeared at a somewhat lower temperature than T_p. The cause of this peak will be discussed later. With the irradiated specimens, polarization tended to occur more as V_b increased. Furthermore, since the sign of the electrode when the poling voltage was applied and the sign of the polarization charge that appeared on the surface of the specimen were opposite, results verified that in all cases the TSC was due to a hetero charge.

Figure 5 shows the results of TSC measurement of specimens irradiated with electron beams, showing only the graph for 100 MGy, which was the highest dose in the experiment. At T_p = 100°C, the TSC peaked near 120°C in the same manner as with non-irradiated specimens. A small peak of about 2 pA also appeared in the vicinity of 175°C. At T_p = 140°C, a TSC peak appeared in the vicinity of 161°C for all values of V_p, while a small shoulder was observed near 175°C. The temperature at which the small shoulder appeared was roughly the same as the TSC peak temperature that appeared on the high temperature side at T_p = 100°C, so these peaks are thought to result from dipole polarization. In other words, ionic space-charge polarization and dipole polarization are believed to occur simultaneously at T_p = 100°C and 140°C. At T_p = 180°C, the value of the TSC peak increases as V_p increases, becoming a single peak. This is thought to be a result of the merging of the two peaks caused by ionic space-charge polarization and dipole polarization. These findings showed that 100-MGy irradiation of electron beams influenced the polarization process. With the irradiated specimens, polarization tended to occur more as V_p increased. Meanwhile, there was no peak due to dipole polarization with non-irradiated specimens, as can be seen in Figure 4. With the non-irradiated specimens, however, spontaneous current began to increase rapidly at a lower temperature than with irradiated specimens. Thus, there is a possibility that the peak caused by dipole polarization is masked by spontaneous current. With irradiated specimens, the TSC peak temperature shifts to a point about 10°C higher than with non-irradiated specimens, as will be described later. One may predicted that, with non-irradiated specimens, a peak due to dipole polarization will appear at around 165°C. In Figure 4, the TSC peak at T_p = 180°C appears at a temperature somewhat lower than T_p. One could predict that, at that time, the peak caused by dipole polarization will appear at a lower temperature than the peak caused by ionic space-charge polarization. From this, the conclusion is that the composite peak of the two peaks seemed to appear at a somewhat lower temperature than T_p.

3.3 TSC peak temperature and peak value

TSC peak temperatures and peak values of non-irradiated and 50, 75 and 100-MGy irradiated specimens were obtained and their dependence on exposure dose and bias voltage was investigated. At T_p = 100°C, each non-irradiated specimen had a peak value no greater than 10 pA. Therefore, they are omitted in this section. Figure 6(a) shows the dependence of the TSC peak temperature on the exposure dose. At T_p = 140°C, the peak temperature gradually shifted to higher temperatures as the exposure dose increased. At T_p = 180°C, the same tendency was seen as at T_p = 140°C, and the magnitude of the peak temperature shift was larger. Figure 6(b) shows the dependence of the TSC peak temperature on V_p. In this figure, very little difference attributable to V_p was seen in a peak

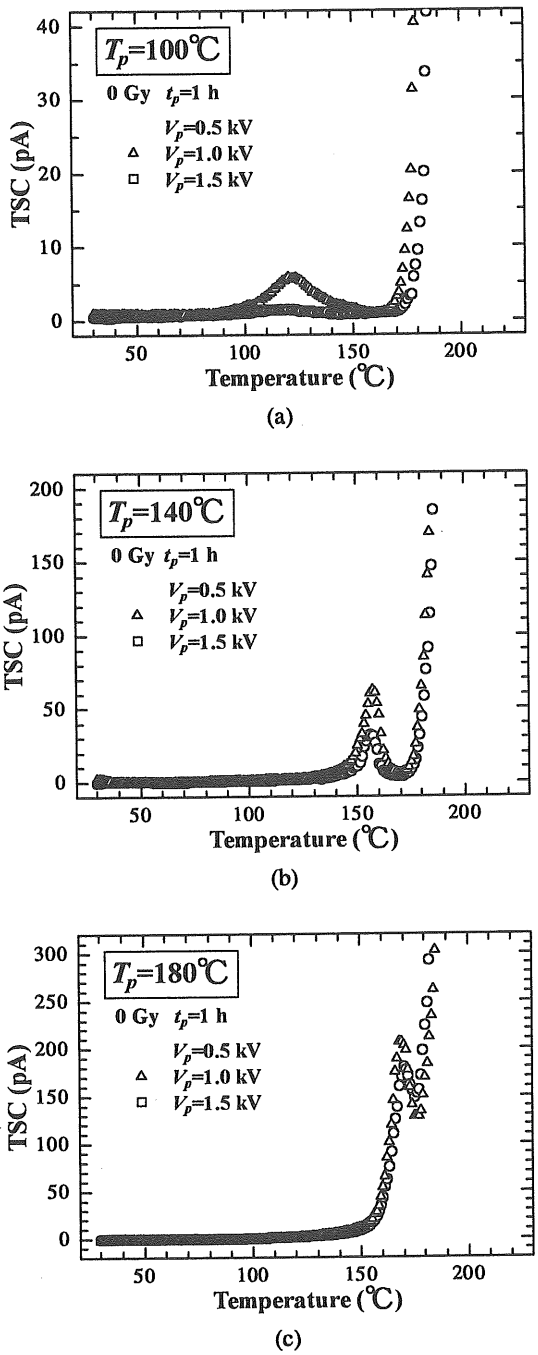

Fig. 4. TSC of non-irradiated specimens.
(a) T_p=100℃, (b) T_p=140℃, (c) T_p=180℃.

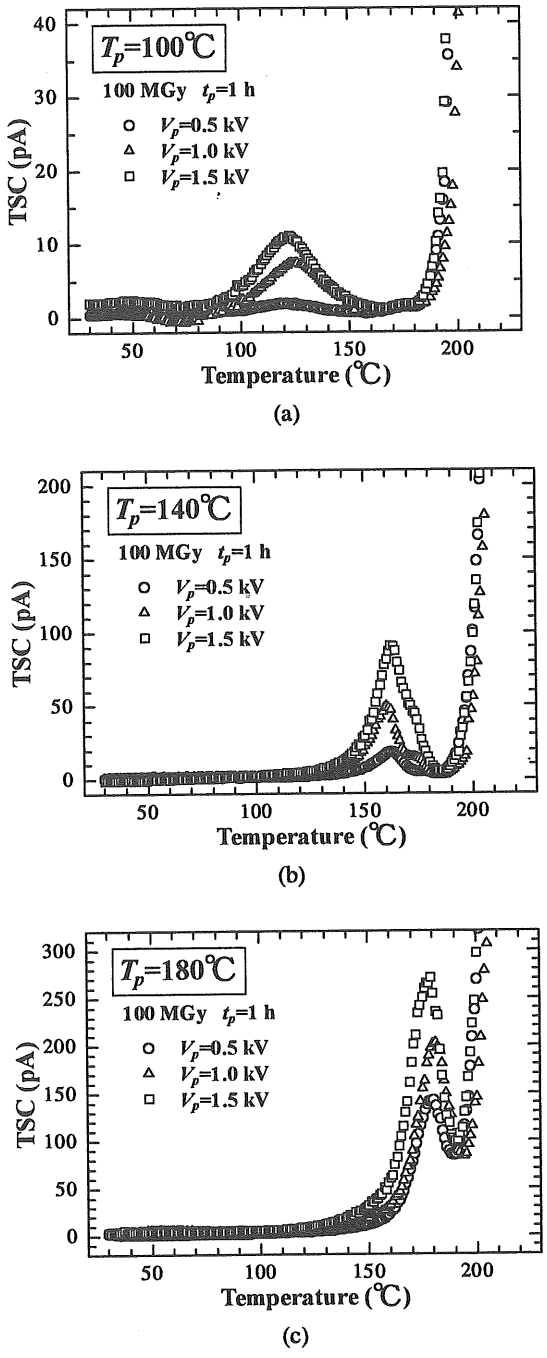

Fig. 5. TSC of 100-MGy irradiated specimens.
(a) T_p=100℃, (b) T_p=140℃, (c) T_p=180℃.

temperature at any T_p. At T_b = 180°C, the peak temperature of irradiated specimens shifted to higher temperatures by about 10°C in comparison to non-irradiated specimens irrespective of the V_p values. That is, the variation in peak temperature due to electron beam irradiation manifested itself remarkably. As can be seen from the results in section 3.1, there is virtually no change in the average free volume (V_{AVE}) due to electron beam irradiation when the specimen temperature is 143°C. At 183°C, however, V_{AVE} decreases along with the irradiation dose. In other words, in the temperature region above T_g, V_{AVE} decreases due to the crosslinking effect caused by electron beam irradiation. Since ionic space-charge polarization and dipole polarization are suppressed, as the irradiation dose rises, the TSC peak temperature shifts to the higher temperature side. Figure 7(a) shows the dependence of the TSC peak value on the exposure dose. At T_p = 140°C, the peak value gradually decreased for higher exposure doses at V_p = 0.5 and 1.0 kV. At V_p = 1.5 kV, however, no difference in peak value was seen between doses. At T_p = 180°C, the peak value of 50-MGy irradiated specimens was larger in

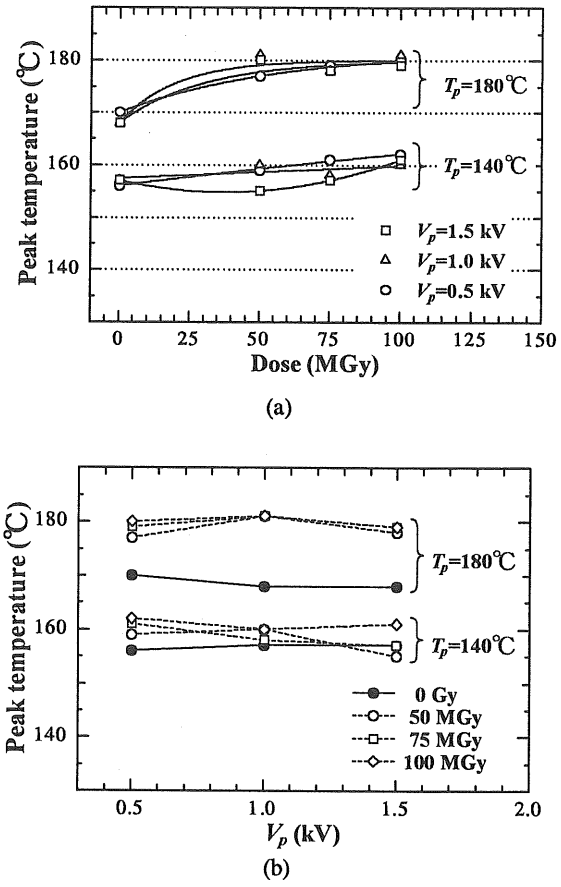

Fig. 6. Dose and poling voltage dependence for the peak temperature.
(a) Dose dependence, (b) Poling voltage dependence.

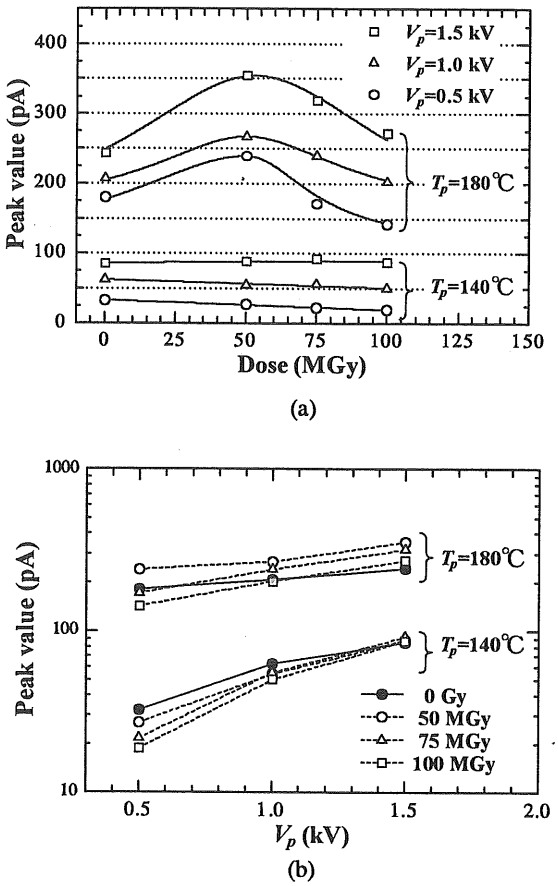

Fig. 7. Dose and poling voltage dependence for the peak value.
(a) Dose dependence, (b) Poling voltage dependence.

comparison to non-irradiated specimens at any V_p. The peak value decreased for doses above 50 MGy. Figure 7(b) shows the dependence of the TSC peak value on V_p. At T_p = 140°C, the peak value increased with an increase in V_p for any specimen and the difference between doses shrank. At T_p = 180°C, the peak value tended to vary with V_p in a similar manner. The increasing rate of the peak value due to V_p was larger with irradiated specimens than with non-irradiated specimens. At V_p = 1.5 kV, the non-irradiated specimens exhibited a minimum.

3.4 Total charge and activation energy

We derived the total charge (Q_{TSC}) and activation energy (H) from the TSC spectra at T_p = 140 and 180°C in order to examine the peak temperature and peak value. The total charge (Q_{TSC}) can be found from Equation (3) where TSC is replaced by $i(T)$.[4] After fitting the TSC spectra by a nonlinear least squares method, and Q_{TSC} can be found from their time integrals.

$$Q_{TSC} = \int_0^{\infty} i(T)dt \qquad (3)$$

Figure 8(a) shows the dependence of Q_{TSC} on the exposure dose. At T_p = 140°C, Q_{TSC} increased with an increase in the dose at each value for V_b. Using an X-ray photoelectron spectroscopic (XPS) analyzer, photoelectron spectra were measured to examine the changes of the specimen's molecular bond states due to electron beam irradiation.[5] The results showed that the bond strength of C-O and C=O increased but that of C-C decreased with an increase in the exposure dose. Apparently, electron beam irradiation collapsed the C-C bonds and the collapsed bonds contributed to the oxidation process. Because exposure doses from electron beams are proportional to exposure time, the oxidation action of the substance due to oxygen in air will continue longer at higher doses. Results demonstrated that the number of dipoles due to oxidation increased with an increase in the exposure dose. In addition, the dependence of conduction direct current on temperature was measured. The results showed that the number of ions increased as a result of electron beam irradiation.[6] At T_p = 140°C, therefore, it is conceivable that polarization is less likely to occur for a higher exposure dose because of crosslinking while Q_{TSC}

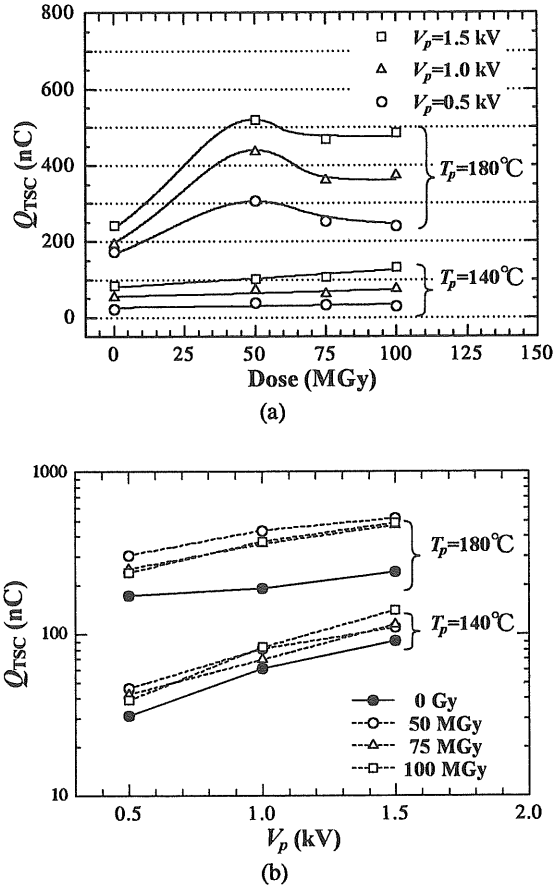

Fig. 8. Dose and poling voltage dependence of total charges.
(a) Dose dependence, (b) Poling voltage dependence.

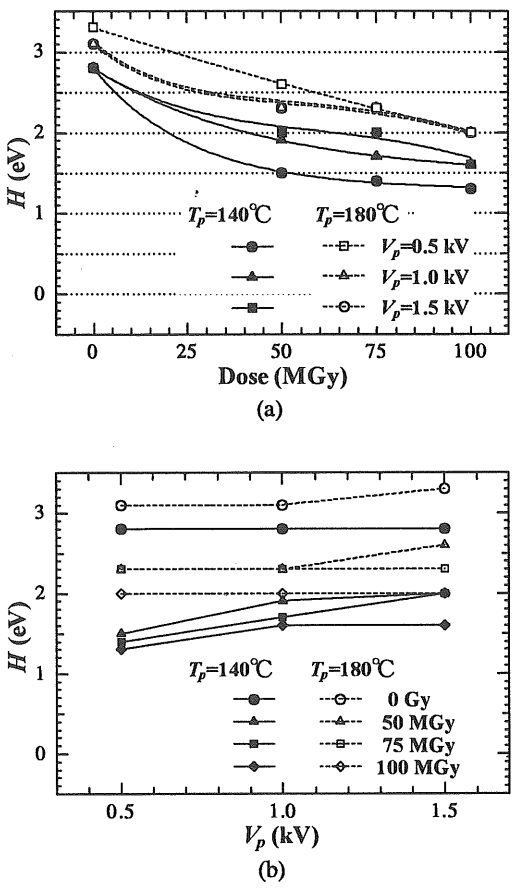

Fig. 9. Dose and poling voltage dependence of activation energy.
(a) Dose dependence, (b) Poling voltage dependence.

increases further with irradiated specimens. At T_p = 180°C, Q_{TSC} is larger with 50-MGy irradiated specimens than with non-irradiated specimens. The results are similar to Fig. 7(a). At T_p = 180°C, because T_p is higher by about 40°C than T_g, the micro-Brownian movement makes the ions in the specimen migrate more. Crosslinking proceeds while the polarization of ionic space charges occurs more readily for a higher exposure dose. Therefore, it is conceivable that the TSC peak value and Q_{TSC} increased more with the 50-MGy irradiated specimens than with the non-irradiated specimens because the former contained a higher number of dipoles and ions. For exposure doses above 50 MGy, Q_{TSC} varied similar to Fig. 7(a). One possible reason for this is that for exposure doses above 50 Mgy, the numbers of dipoles and ions increased but crosslinking was promoted at the same time, so the TSC peak value and Q_{TSC} decreased.

Figure 8(b) shows the dependence of Q_{TSC} on V_p. Q_{TSC} increased with an increasing V_p regardless of T_p and the non-irradiated specimens exhibited the minimum. At T_p = 180°C, in particular, the irradiated specimens had values that were 1.4 to 2.4 times as high as the non-irradiated specimens. From these results, it is obvious that electron beam irradiation increased the amount of the charge.

From the initial rise of TSC spectra, the dependence of the activation energy on the exposure dose was investigated at each value T_p. Activation energy (H) can be found by plotting ln $i(T)$ against $1/T$ (Arrhenius plot) using the relationship for Equation (4) and from the slope H/k of the plot:[4]

$$\ln i(T) = i_0 - \frac{H}{kT} \tag{4}$$

where, i_0 is a constant, k is Boltzmann's constant, and T is the absolute temperature.

Figure 9(a) shows the dependence of H on the exposure dose. H decreased with an increase in the exposure dose regardless of T_p. In non-irradiated specimens, dipoles and ions can be polarized, but this is impossible in irradiated specimens because of the crosslinking effect of electron beam irradiation. Therefore, the energy H of depolarization is believed to be smaller with irradiated specimens. H was larger at

T_p = 180°C than at T_p = 140°C. This implies that a larger polarization occurs at a higher T_p, so depolarization involves a larger H. This tendency remained the same when V_p varied.

Figure 9(b) shows the dependence of H on V_p. At T_p = 140°C, the non-irradiated specimens showed no variations in H due to V_p while H for 50 and 75 MGy tended to increase with an increase in V_p. H for 100 MGy increased in the section from V_p = 0.5 to 1.0 kV. In the case of T_p = 180°C, no variations were seen in H in the section from V_p = 0.5 to 1.0 kV with any specimen. Up to V_p = 1.5 kV, H for 75 and 100 MGy did not vary. In short, H of irradiated specimens tended to increase with V_p when T_p = 140°C, but did not vary significantly when T_p = 180°C. Crosslinking seems to be involved in this, but the details are as yet unknown.

4. Conclusions

Polyetheretherketone (PEEK) was irradiated with electron beams at high doses, and the longest-living component of the positron lifetime (τ_3) and thermally-stimulated current (TSC) were measured to investigate the internal structural changes in the specimen and their influence on its electrical properties. The results are summarized as follows:

(1) Measurements of positron lifetime showed that τ_3 began to rapidly increase from T_g with the non-irradiated specimens but the rate of increase for τ_3 decreased from T_g on with regard to the 50 and 100-MGy irradiated specimens.

(2) The TSC peak temperature of the irradiated specimens shifted to higher temperatures and the peak temperature difference between irradiated and non-irradiated specimens grew larger for a higher T_p regardless of V_p.

(3) When T_p = 140°C, the TSC peak value gradually decreased with an increase in the exposure dose at V_p = 0.5 and 1.0 kV, but no difference was seen between doses at V_p = 1.5 kV. At T_p = 180°C, the peak value was higher with the 50-MGy irradiated specimens than with the non-irradiated specimens for any V_p, but decreased for doses above 50 MGy.

(4) The total charge (Q_{TSC}) increased further with the irradiated specimens and an increase in V_p when T_p = 140°C. When T_p = 180°C, it exhibited the same tendency as for variations in the TSC peak value.

(5) Activation energy (H) decreased with an increase in the exposure dose at any T_p. H for T_b = 180°C is large in comparison to T_p = 140°C and exhibited a similar tendency when V_p varied.

We thank Professor T. Suzuki in the High Energy Accelerator Research Organization and M. Baba, a member of the technical staff at the college, for their assistance with experiments. We also wish to thank Professor M. Ruike at the Hachinohe National College of Technology for his help with the instrumentation. Part of this research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Sports, and Culture.

References

1) K. Shiraishi, T. Kinoshita, H. Yamaoka, and A. Kayama: *Irradiation Effects in Materials*, p.168, Shokabo, Tokyo (1994)
2) K. Shinyama, T. Suzuki, and S. Fujita: Trans. IEE of Jpn, 116-A, (1996) 279
3) T. Suzuki, Y. Oki, M. Numajiri, T. Miura, K. Kondo, and Y. Ito: Polymer, 34 (1992) 1361
4) T. Hino, K. Yamashita, and F. Kaneko: Proc. Inst. Electrostat. Jpn, 4 (1980) 252
5) S. Fujita, K. Shinyama, T. Suzuki, and M. Baba: Proc. ISANER (1997) 279
6) K.Shinyama, M.Baba, and S.Fujita: Proc. J-K Joint Symp. ED and HVE (1997) 213