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Damage-depth profiling of an ion-irradiated polymer by monoenergetic positron beams

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Poly(aryl-ether-ether ketone) (PEEK) films irradiated with 1-MeV and 2-MeV O^+ ions were exposed to positron beams to measure the positron annihilation Doppler broadening as a function of the positron energy. The annihilation lines recorded at relatively low positron energies were found to become broader with increasing irradiation dose, suggesting that positronium (Ps) formation is inhibited in the damaged regions. The positron data were compared with the results of dynamic hardness and electron-spin-resonance measurements. The slow-positron Doppler broadening technique is found to be a useful means for damage-depth profiling of Ps-forming polymers.

I. INTRODUCTION

Ion implantation is a useful technique to modify polarity, electron conductivity, and other surface properties of organic polymers. Implanting ions by irradiation, however, sometimes causes significant radiation damage, resulting in the final sample structure and composition much different from those of the original material.[1]

Variable-energy positron beams, in combination with the Doppler broadening technique, have been successfully applied to damage and defect depth-profiling of metals and semiconductors.[2,3] The positrons injected into these materials strongly interact with the defects, resulting in a reduced Doppler broadening of the annihilation γ rays with an energy of 0.511 MeV each. The usefulness of this technique, however, for the study of organic polymers has not been explored. Positron annihilation in polymers is known to be more complex than it is in metals and semiconductors, because a certain fraction of the positrons can abstract an electron to form a hydrogenlike bound state called positronium (Ps).[4,5] Ps can exist either in the singlet *para*-positronium (*p*-Ps) or the triplet *ortho*-positronium (*o*-Ps) state. Normally *p*-Ps and *o*-Ps are formed in the ratio of 1 to 3. The formation and annihilation of Ps varies from one substance to another, being sensitive to the free volume as well as to the presence of chemically active species, such as free radicals. In this paper, we report our attempt of using this positron beam Doppler broadening technique to perform damage-depth profiling of an ion-irradiated polymer.

The sample chosen for the present work was poly(aryl-ether-ether ketone) (PEEK), a radiation resistant polymer with a high glass transition temperature of about 140 °C. Semicrystalline PEEK films were irradiated with 1-MeV and 2-MeV oxygen ions (O^+) up to a dose of 6×10^{13} ions/cm^2. Doppler broadening of the annihilation γ rays was measured with a positron beam system as a function of the incident positron energy. The positron data were compared with the results of dynamic hardness measurements and free radical concentrations determined by electron spin resonance (ESR).

II. EXPERIMENT

Our slow positron beam system is shown in Fig. 1. Energetic positrons emitted from a sealed ^{22}Na source with an activity of 1.11 GBq (from Amersham) are moderated by a polycrystalline tungsten foil with a thickness of 6 μm. The moderator was prepared in *in situ* annealing at 2000 °C under a vacuum better than 10^{-4} torr. Monoenergetic positrons coming from the other surface of the moderator, because of the negative positron work function of tungsten,[2] are separated from high-energy positrons by a curved $\mathbf{E}\times\mathbf{B}$ filter[6] and guided to the sample by a uniform longitudinal magnetic field of about 0.01 T. The sample chamber and the beam line are electrically separated, so that the beam energy can be varied by simply floating the beam line and the source chamber to a desired electrostatic potential.

Semicrystalline PEEK films with a thickness of 25 μm and a density of 1.285 g/cm^3, which were kindly supplied by Sumitomo Chemical Co. Ltd., were irradiated with 1-MeV and 2-MeV O^+ ions up to a dose of 6×10^{13} ions/cm^2 with an electrostatic ion accelerator (2-MeV model, High Voltage Engineering, Europe). The ion current densities were between 3 and 8 nA/cm^2. The implantation depths of the oxygen ions with 1-MeV and 2-MeV energies were calculated by the TRIM code[7] and

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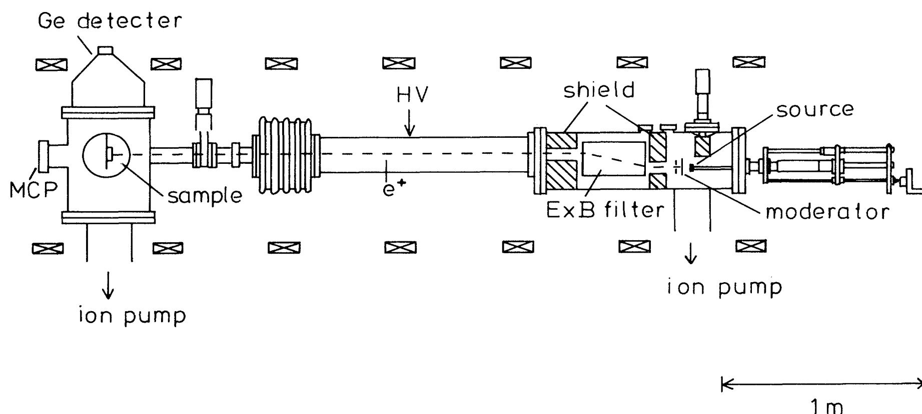


FIG. 1. Variable-energy positron beam system. Annihilation γ rays are detected from one side of the sample chamber.

were found to be 1.7 and 2.6 μm, respectively (Fig. 2). The positron annihilation Doppler broadening was measured as a function of the positron energy (E) from 80 eV up to 35 keV by an intrinsic Ge detector with high-energy resolution (EG&G Ortec GEM10175P). During the measurement, samples were kept under a vacuum of the order of 10^{-8} torr. The data were analyzed in terms of the S parameter, which is the ratio of γ-ray counts in the central part of the 0.511 MeV annihilation peak to the total counts contained in the whole peak. The S parameters were found to be unaffected by any charging up effect due to positron irradiation.

Dynamic hardness measurements were carried out with a dynamic ultra-microhardness tester, Shimadzu DUH-201S. A triangular pyramid indenter (115°) was pressed against the specimen by electromagnetic force. The pressing force was increased linearly from zero to a set point value of 0.5 or 10 g, held at the value for 5 s and the indentation depth was automatically measured. The dynamic hardness (DH) was determined by using the relation[8]

$$\mathrm{DH}=37.838P/D^2 ,$$

where P is the set point load in grams and D is the indentation depth in μm.

ESR spectra were recorded with JEOL JES-RE3X spectrometer operated at a microwave frequency of 9.43 GHz and a magnetic field modulation of 100 kHz. A symmetric signal with a peak-to-peak separation of about 0.7 mT was observed. The signal intensities were obtained by numerical double integration and diphenylpicrylhydrazyl was used as the standard for converting the intensity to the spin density.

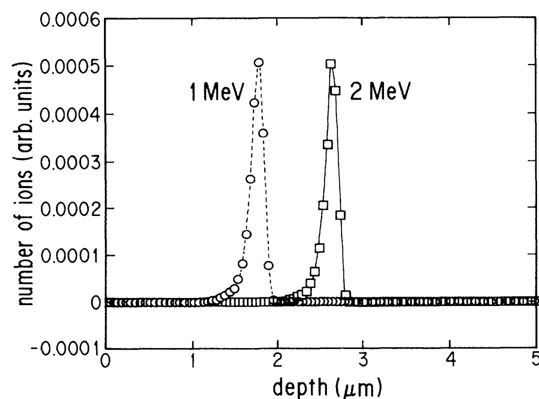


FIG. 2. Implantation profiles of O^+ ions in PEEK calculated by the TRIM code. ○: 1 MeV irradiation; □: 2 MeV irradiation.

III. RESULTS

S-E curves for unirradiated and irradiated PEEK samples are shown in Fig. 3. The upper horizontal axis indicates the average positron implantation depth obtained by the formula[3]

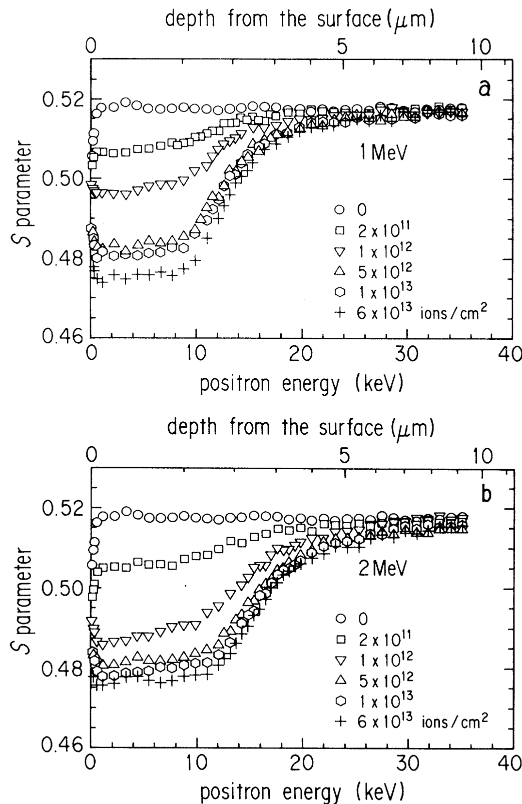
$$\langle z \rangle=(0.04/\rho)E^{1.6} ,$$

where $\langle z \rangle$ is the average positron implantation depth in μm, E is the incident energy in keV, and ρ is the material density in g/cm^3. The S parameters observed at relatively low positron energies become lower with increasing irradiation dose, a result in contrast to the case of irradiated metals and semiconductors, where the positron trapping by the defects causes a narrowing of the annihilation peak. It is seen in the figure that the region, where the reduced S parameters are observed extends deeper for the samples irradiated with 2-MeV ions than those irradiated with 1-MeV ions. This is in parallel with the implantation depths calculated by the TRIM code: 1.7 and 2.6 μm for the 1-MeV and 2-MeV ions, respectively.

The implantation profile of positrons $P(z,E)$ is often approximated by the relation[3]

$$P(z,E)=-\frac{d}{dz}[\exp(-z^2/z_0^2)] ,$$

where $z_0=(0.045/\rho)E^{1.6}$. For PEEK, z_0 is only 0.035 μm at 1 keV but at 20 keV it is 4.2 μm. This illustrates that the positron implantation profile becomes increasingly broader with incident energy. The depth dependence of S parameters of Fig. 3 is, thus, considerably distorted. We assumed that the unfolded depth profile can be approximated to a step function. The width and depth



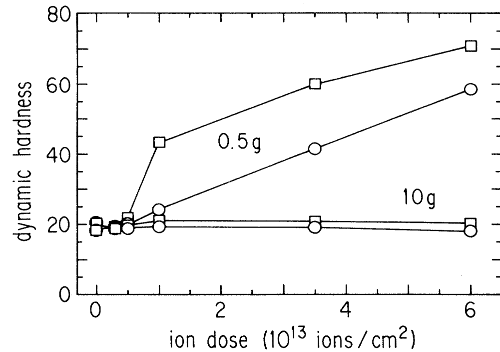


FIG. 5. Dynamic hardness obtained with set point loads of 0.5 and 10 g as a function of the ion dose. Symbols as in Fig. 2.

of the step as well as the bulk S parameter were fitted by means of a simple least-square analysis. Results of the fitting are shown in Fig. 4. Effect of positron or Ps diffusion was not taken into consideration because the experimental data for the unirradiated sample deviate from the bulk S value only in the region $E < 1$ keV, suggesting low diffusivity.[9,10] The S values of the unfolded profiles are reduced in the region $z < 1.9$ μm (1 MeV) or 2.7 μm (2 MeV), revealing that the polymer is damaged only in the near-surface region, where the energetic ions passed through. It appears that the S parameters are reduced as a result of ionization rather than the elastic collisions of incoming oxygen ions.

In Fig. 5 are shown variations of dynamic hardness as a function of the irradiation dose. The indentation depths of the indenter, for the set point loads of 0.5 and 10 g, are 0.52–1.0 and 4.2–4.5 μm, respectively. Therefore, while the near surface dynamic hardness starts to increase at a dose around 1×10^{13} ions/cm^2, the hardness inside the polymer is unchanged. This agrees with the positron result in Fig. 4, because the latter indicates that the polymer is damaged only in the near-surface layer. The increase of the hardness may be due to carbonization of the damaged layer.[11] Laser Raman spectra of samples with doses higher than 3.5×10^{13} ions/cm^2 exhibited

FIG. 3. S-E curves for PEEK irradiated with O^+ ions of (a) 1 MeV and (b) 2 MeV. The positron energy was varied from 80 eV to 35 keV.

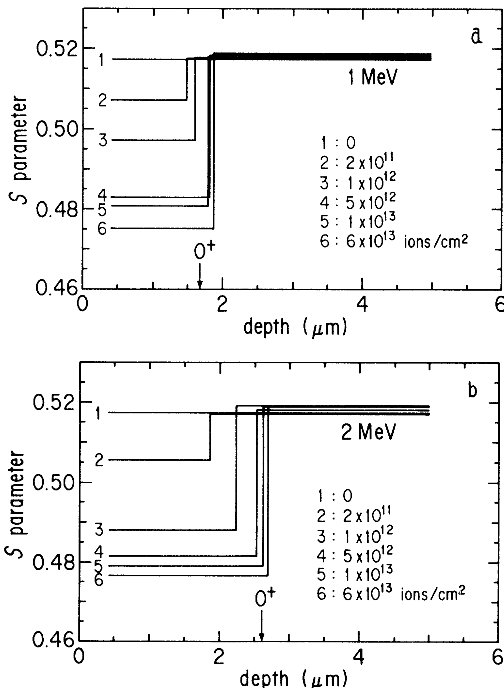


FIG. 4. Unfolded depth profiles. (a) with 1 MeV irradiation, (b) with 2 MeV irradiation. S parameters at positron energies below 1 keV were not included in the analysis.

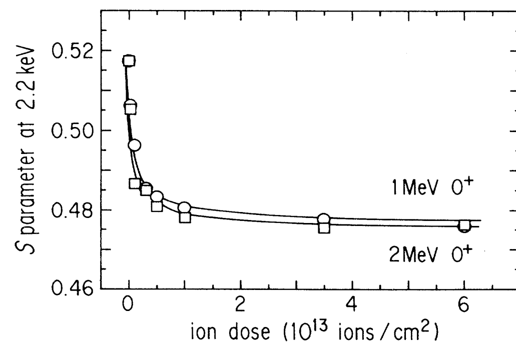


FIG. 6. S parameters at the positron energy of 2.2 keV as functions of irradiation dose. Symbols as in Fig. 2.

broad peaks at 1600 and 1360 cm^{-1}, pointing to the formation of glassy carbon.

In order to see how the S parameter in the damaged region varies as a function of the dose, we plotted the S parameter at a positron energy of 2.2 keV, corresponding to an average depth of 0.1 μm from the surface, versus the ion dose, Fig. 6. The S parameters for both sets of the samples, irradiated with the 1-MeV and 2-MeV ions, exhibit sharp decreases until the dose reaches 1×10^{13} ions/cm^2. At doses higher than 1×10^{13} ions/cm^2, the S values are nearly constant around 0.48, which is close to the value for Kapton with no Ps formation.

IV. DISCUSSION

Since the self-annihilation of p-Ps atoms results in a very low momentum of the annihilating pair and gives a sharp annihilation peak with a large S value, the S parameter is well correlated with the number of Ps atoms formed in a polymer. It has been confirmed that some positrons do form Ps in unirradiated PEEK;[12] the fraction of o-Ps atoms in our pristine sample was about 18%.[13] Besides, Suzuki *et al.*[14] studied unirradiated and O^{2+} (3-MeV)-irradiated polyethylene terephthalate films by the slow-positron lifetime technique and reported that the o-Ps yield in the damaged layer of the irradiated sample (dose$=5\times10^{13}$ ions/cm^2) is almost zero. Our results in Fig. 6 suggest that with increase in the irradiation dose the Ps fraction of PEEK decreases and at 1×10^{13} ions/cm^2 it becomes zero. Here one should note that the change of the S parameters in the damaged region is already significant even at a dose as low as 2×10^{11} ions/cm^2, which is only one-fiftieth of the dose required for the hardness to change (Fig. 5). The positron techniques may be useful to detect irradiation damage of Ps-forming polymers in its early stage.

As the S parameter appreciably decreases at low doses, it is reasonable to attribute the change of the S parameter to a chemical effect rather than a change in the polymer structure or the free volume. Two different models, the Ore model and the spur model, have been proposed to account for Ps formation in molecular substances. The Ore model[15] postulates that Ps is formed through direct electron abstraction from medium molecules during slowing down of the energetic positron. Ps formation through this process is most efficient when the positron energy lies in the range from E_{ex} down to I_p-I_{Ps}, where E_{ex} and I_p are, respectively, the lowest excitation energy and the ionization energy of the medium molecule and I_{Ps} is the binding energy of Ps. I_{Ps} is written as 6.8 eV-E_{zero}, where 6.8 eV is the Ps binding energy in vacuum and E_{zero} is the quantum mechanical zero-point energy of localized Ps in a polymer. If $E<I_p-I_{Ps}$, the positron energy is not sufficient to abstract an electron from the molecule. On the other hand, if $E>E_{ex}$, excited-state formation is supposed to be more probable than the Ps formation. One should note that the lower threshold of Ps formation may be lowered at the surface because $E_{zero}\sim0$. In the spur model Ps formation is assumed to take place via recombination of the thermalized positron and one of electrons, released by the position itself, in the terminal positron spur.[16] In this case Ps formation must compete with other processes like positron and electron scavenging, electron-ion recombination, positron and electron escaping from the spur, etc. In either case, scavenging of precursors of thermalized Ps atoms, such as free electrons, a positron and/or hot Ps atoms, lead to a reduction of the Ps yield, i.e., the inhibition of Ps formation. Many authors studied γ- or electron-irradiated substances by the conventional positron annihilation techniques and explained the reduced Ps formation in terms of the scavenging or chemical effect of free radicals.[17–22]

Figure 7 shows the S parameter at the positron energy

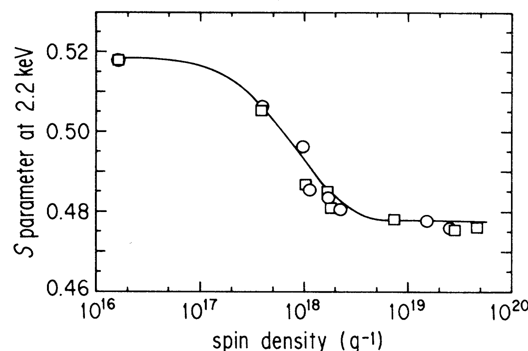


FIG. 7. S parameters at 2.2 keV as functions of spin densities in the damaged regions for O^+-irradiated PEEK. Symbols as in Fig. 2.

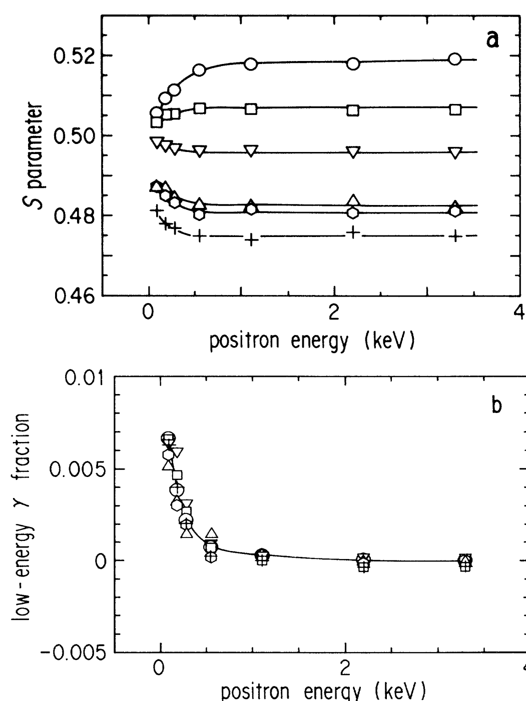


FIG. 8. (a) S parameters and (b) low-energy (410–490 keV) fraction of γ rays as functions of incident positron energy (80 eV–3.3 keV) for PEEK irradiated with 1 MeV O^+ ions. In (b), background level was taken to be 30 keV. Symbols as in Fig. 3.

of 2.2 keV as a function of the average spin density obtained by ESR. It was assumed that free radicals were uniformly distributed from the surface down to the penetration depths of the irradiated ions, 1.7 or 2.6 μm, and no radicals were produced beyond them. There seems to be a correlation between the two quantities; data points for both 1-MeV and 2-MeV irradiation are reproduced by a single curve rather well. However, annealing of an irradiated sample at a nominal temperature of 220 °C ($> T_g$) for 10 h under vacuum did not change the S-E curve significantly, whereas the spin density determined by ESR showed some 50% decrease. Furthermore, as was pointed out by Eldrup, Lund-Thomsen, and Mogensen,[18] spin densities of irradiated substances are much lower than the concentrations of ordinary Ps inhibitors required to reduce the Ps yield to the same extent. Probably, radicals are not the only species responsible for the inhibition;[18] oxidized species produced by a reaction between oxygen and radicals[22,23] as well as some polar groups formed as the result of irradiation[18] may also contribute to the Ps inhibition.

Returning to the S-E curves, it is interesting to note that at incident energies below 1 keV, S parameters for ion doses 0 and 2×10^{11} ions/cm^2 increase, while those for higher doses decrease, with increasing the positron energy. Figure 8(a) shows S-E curves for PEEK irradiated with 1 MeV ions and probed with low-energy positrons. It appears that Ps yields at the surface are less affected by the ion irradiation. In order to get additional information on the yield of o-Ps atoms formed at the surface, we evaluated the fraction of γ-ray counts in a range between 410–490 keV as a function of the positron energy, Fig. 8(b). The o-Ps atoms coming from the surface annihilate into 3γ quanta in vacuum, thereby increasing the low-energy fraction of the γ-ray spectrum. The data in Fig. 8(b) thus show that the yield of the surface o-Ps increases to a constant value with decreasing positron energy, without being affected by the ion irradiation.

The higher yield of o-Ps coming out from the surface at lower positron energies may be due to increased positron interaction with the surface. Low-energy positrons should have higher probability to interact with the surface and pick up an electron to form Ps, without being affected by the presence of scavengers in the polymer. With increasing incident energy, more and more positrons pass through the surface and no Ps comes out from the surface above 1 keV. On the contrary, the Ps yield in the polymer may increase or decrease with incident energy, depending on the Ps yield at high energies. The increase of the S parameter with incident energy for the unirradiated PEEK, for example, may be ascribed to increased Ps formation by the spur processes. The number of ionized electrons generated by a positron increases with the incident energy. As a result, the number of thermalized electrons with which a positron can combine to form Ps increases and Ps formation is enhanced. This is similar to the explanation given by Eldrup *et al.*[9,10] for Ps formation in ice at energies below 1 keV. In the case of a sample with a low Ps yield such as heavily irradiated PEEK, the Ps yield decreases with energy, because the Ps formation at energies above 1 keV is already suppressed by the inhibition effect.

V. CONCLUSION

The slow positron Doppler broadening technique is useful for nondestructive damage-depth profiling of Ps-forming polymers as well as for the study of Ps formation in polymers. In the present study, positron annihilation Doppler broadening was measured for O^+-irradiated PEEK as a function of the positron energy. The observed decrease of the S parameters at relatively low positron energies was attributed to the inhibition of Ps formation due to active species formed by irradiation. Ps atoms formed at the surface were studied through the 3γ annihilation measurements and found to be little affected by the ion irradiation.

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