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ARTICLE

Characterization of ion-irradiated Poly-L-Lactic Acid using nano-cutting

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Effects of the irradiation of 150 keV He^+ ion on the mechanical strength of poly-L-lactic acid (PLLA) were studied. Change of the irradiated surface was investigated by a surface texture and contour measuring instrument and an atomic force microscope. Observation by the atomic force microscope revealed that the irradiated surface significantly subsided as the fluence increases. In order to investigate the dependence on fluence of the depth of the Bragg peak of the ion implantation, cutting strength, Σ, [F. Saito, I. Nishiyama and T. Hyodo, *Materials Letters*, **66**, 144-146 (2012)], an indicator for the strength of materials against cutting obtained from cutting resistance was analyzed. The averaged ion projected range increased from about 1.1 μm for a fluence of 1×10^{15} He^+/cm^2 to about 4μm for a fluence of 1×10^{16} He^+/cm^2. The density of the irradiated part after irradiation was estimated by a combination of cutting resistance measurements and positron annihilation γ ray Doppler broadening measurements using an energy-variable positron beam. The density decreased from the value before irradiation, 1.27 g/cm^3, to about 0.6 g/cm^3 after the irradiation to a fluence of 3×10^{15} He^+/cm^2. Taking into account the decrease in the density and the subsidence of the surface, it is concluded that only 30 % of the weight remained in the irradiated region after the irradiation. Anisotropic change in the cutting resistance suggests that mechanical strength in the direction normal to the surface increased while that in the lateral direction became rather fragile.

Introduction

Ion irradiation is widely used for modifying surfaces of metals, ceramics, semiconductors and polymers. In the case of polymers, cleaving and crosslinking are main process at low fluences. Cleaving is the result of ruptures of chemical bonds with reduction of the average size of molecular chains, so that various kinds of volatile products are ejected from the surface. [1-3] Crosslinking is the recombination process of the cleaved bonds involving formation of double or triple bonds in the irradiated parts. These processes inevitably affect the density and the mechanical properties of the irradiated part of the polymer. Since polymers are highly sensitive to ion irradiation in comparison with metals, ceramics and semiconductors, ion-beam-modified polymers are used in many areas, such as medical purposes, optics and electronics. However, it is still open to intensive researches including change of density and mechanical strength of irradiated part for more comprehensive applications. For the effect of swift ion irradiation with energy of ~ MeV, a stack sample of thin polymer films was investigated using infra-red spectroscopy and/or Raman spectroscopy. [4-6] Observed increase with fluence in the depth of the affected region was attributed to decrease in the density of the irradiated part by the ejection of volatile products during irradiation. However, for the investigation of the effects by ion irradiation with energy of ~100 keV, it is difficult to use stacking films since the ion implantation depth is too small.

In the present work, the near surface region of poly L-lactic acid (PLLA) irradiated by He^+ ions with an energy of 150 keV has been studied by cutting resistance and positron annihilation γ ray Doppler broadening, a surface texture and contour measuring instrument, STMI, and an atomic force microscope (AFM). Owing to novel combinations of these methods, it has been possible to investigate density and mechanical strength of the irradiated PLLA qualitatively. PLLA is a biodegradable polymer synthesized from alpha hydroxyl acid family and used for bio-compatible substitutes. Adhesiveness of PLLA surface to bio-cell is enhanced by ion irradiation as is the case with many polymers.[7,8]

Experiments

Sample plates of 10×10 mm^2 for the SAICAS measurements were cut from a sheet of 0.2 mm thick LACTY (Shimadzu) whose density and molecular mass were 1.27 g/cm^3 and 120000-140000, respectively. They were irradiated by He^+ ions with an energy of 150 keV using a 200 kV low-current implanter at RIKEN to fluences of 3×10^{14}, 1×10^{15}, 3×10^{15} and 1×10^{16} He^+/cm^2 at room temperature. The diameter and the current of the He^+ ion beam were about 35mm and 0.05 μA, respectively. During the irradiation, the samples were covered with a stainless steel mask plate 2mm thick with an opening of 8×8 mm^2 and kept electrostatically grounded. The irradiated part of the samples got slightly coloured to opaque brown with increase in fluence.

The surface around the boundary between the irradiated part and the masked part was inspected with an atomic force microscope, AFM (JSPM-4200, JEOL). Since the scanning range of AFM is not large enough, the planarity of the irradiated surface was inspected by using a surface texture and contour measuring instrument, STMI (SURFCOM 1400D, ACCRETECH) for a sample irradiated with a narrow stainless steel mask plate with a slit 0.2 mm wide.

Cutting resistance was measured using a nano-cutting analysis machine, Surface and Interfacial Cutting Analysis System (SAICAS, NN-40, Daipla Wintes Co. Ltd.). This apparatus cuts a sample mechanically, controlled with an accuracy of 5 nm, and detects the components of cutting resistance of the sample parallel to and perpendicular to the surface with an accuracy of 1.2 mN. A cutting tool made of diamond single crystal 0.3 mm wide was used. The rake angle and the clearance angle of the cutting tool were 20° and 10°, respectively. The edge of the cutting tool was straight. The PLLA samples were fixed on slide glasses with cyanoacrylate adhesive and then placed on the suction-type chuck of the apparatus. The cutting tool was initially positioned ~ 0.1 μm above the surface of the sample, which was checked using an optical microscope. It moved at a horizontal speed of 500 nm/s and a vertical speed of 30 nm/s, which made a cutting angle of 3.4°. Cutting was made down to a depth of 9μm, corresponding to the lateral displacement of 150 μm.

Measurements of positron annihilation γ ray Doppler broadening spectroscopy, DBS, using a slow positron beam [9] were performed on an as-received sample and a sample ion-irradiated to the fluence of 3×10^{15} He^+/cm^2. During the He^+ ion irradiation, the sample plate of 30×30 mm^2 were covered with a stainless steel mask plate with an opening of 20×20 mm^2. The opening area was large enough that the positron beam of diameter about 4mm was directed easily on the central part of the irradiated region. The energy of the incident positron beam ranged from 0.1 to 30 keV. Since a tungsten mesh moderator was used, energy spread of the beam was about 1 eV larger than that provided by a tungsten foil moderator. The 511 keV γ rays from the annihilation of positron and electron pairs were detected with a Ge detector. Details of the beam apparatus is described elsewhere [10]. The data was analyzed in terms of the shape parameter (S-parameter) and the wing parameter (W-parameter). The former is defined as the ratio of the counts of a central region to the total counts of the energy peak of the 511 keV annihilation γ rays [11] and the latter as the ratio of the counts in wing regions of the both sides to the total counts. In the present work, the energy peak extended from -177 to +177 channels centered at 0 channel; the central region for the S-parameter was chosen to be -20 to +20 channels. The wing regions for the W-parameter were chosen to be from -177 to -57 and from +57 to +177 channels.

Results

Figure 1 shows an AFM image of the border of the part irradiated to a fluence of 1×10^{15} He^+/cm^2. The left hand side of the image is the masked part and the right hand side is the irradiated part. The level of the irradiated surface has subsided by 0.75 μm from the original level (the masked part). The subsidence increased from 0.3 μm for the sample with a fluence of 3×10^{14} He^+/cm^2 to 1.3 μm for the sample with a fluence of 3×10^{15} He^+/cm^2. A valley-like narrow gap is also observed. The gap was too narrow to be measured to the bottom with AFM. The gap got wider and deeper with fluence. The results with STMI showed that the irradiated surface other than the gap on both edges was nearly flat.

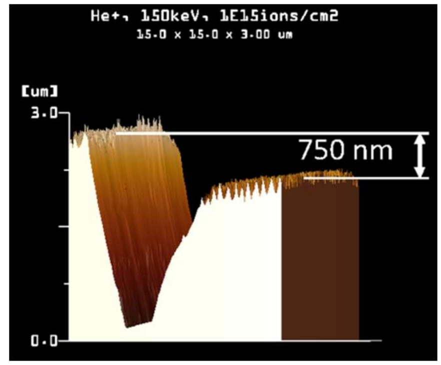


Figure 1 AFM image of the boundary of irradiated surface with a fluence of 1×10^{15} He^+/cm^2.

The cutting resistance parallel to the surface, F_h, and that perpendicular to the surface, F_v, averaged over three runs of measurements with the SAICAS for the samples as-received and those irradiated to fluences ranging from 3×10^{14} He^+/cm^2 to 1×10^{16} He^+/cm^2 are shown in Figure 2 as functions of the depth. The depth was measured from the position where the cutting tool touched the surface as determined by detecting sudden increase in F_v from zero. For the as-received sample (figure 2(a)), F_h and F_v increase linearly with depth as expected, except in the region very close to the surface. In this region, the cutting tool deformed the surface before cutting in. For the irradiated samples (figure 2(b)–2(e)), F_h and F_v vary in a complex way. In addition, the cutting tool cut into the sample easily with negligibly small deformation of the surface. The mechanical property near the surface appears to have changed.

Figure 3 shows the incident positron-energy dependence of the S-parameter of the positron annihilation γ ray Doppler broadened spectra for the samples irradiated to a fluence of 3×10^{15} $ions/cm^2$ and the as-received sample. The abscissa shows incident positron energy. The S-parameter for the as-received sample was almost constant. In contrast, that for the irradiated sample showed explicit decrease below the energy, E_p, of about 10 keV. The decrease in the S-parameter indicates that the low momentum component of the Doppler broadened peak for the annihilation γ rays decreased by the ion irradiation. Figure 4 shows the correlation of S- and W-parameters, where ordinate is S-parameter and abscissa is W-parameter. They have a simple negative correlation. The changes in the S- and W-parameters are caused by the change of the electronic property of the irradiated part induced by the change in the structure due to the ion irradiation. The decrease in the S-parameter shown in figure 3 and the accompanying increase in W-parameter shown in figure 4 is reasonably explained by a reduction of the positronium formation fraction, though the detailed mechanism is not necessary for the analysis below.

The recovery of the S-parameter for E_p larger than 15 keV suggests that most of the positrons injected with such energy annihilate in the un-irradiated region. The end point distribution for the implanted positrons is wider than that of the ions, since the mass of the former is more than three orders of magnitude smaller than that of the latter. Thus S-parameter obtained is an average of the values over the region where the positrons distribute and annihilate. When the surface region is affected by irradiation, it is expected that S-parameter varies continuously with incident positron energy. Thus the value of E_p which corresponding to the middle value of S-parameter, about 8 keV, is interpreted as that the positrons implanted with which energy annihilate around the Bragg peak of the ion implantation.

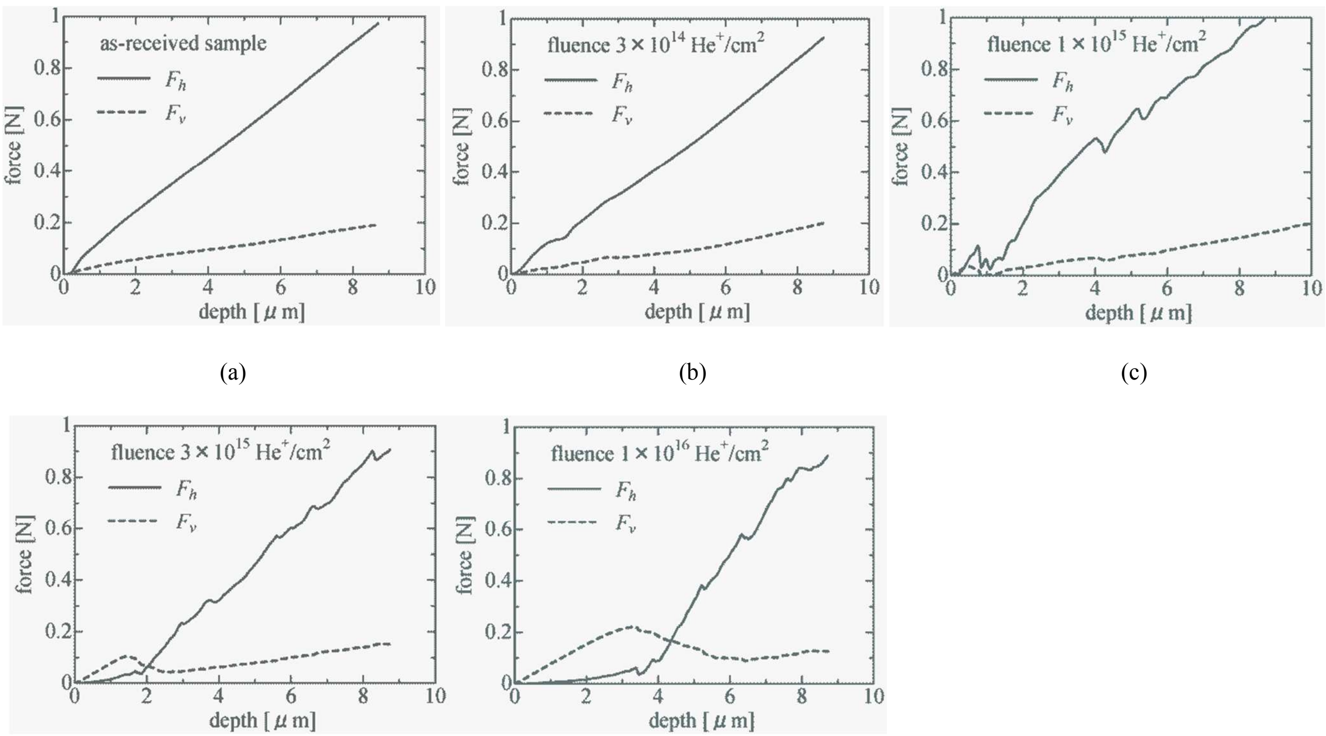


Figure 2 Components of the averaged cutting resistance obtained by three independent measurement runs are shown as functions of depth; (a) as-received. (b) with a fluence of 3×10^{14} He^+/cm^2, (c) 1×10^{15} He^+/cm^2, (d) 3×10^{15} He^+/cm^2, and (e) 1×10^{16} He^+/cm^2.

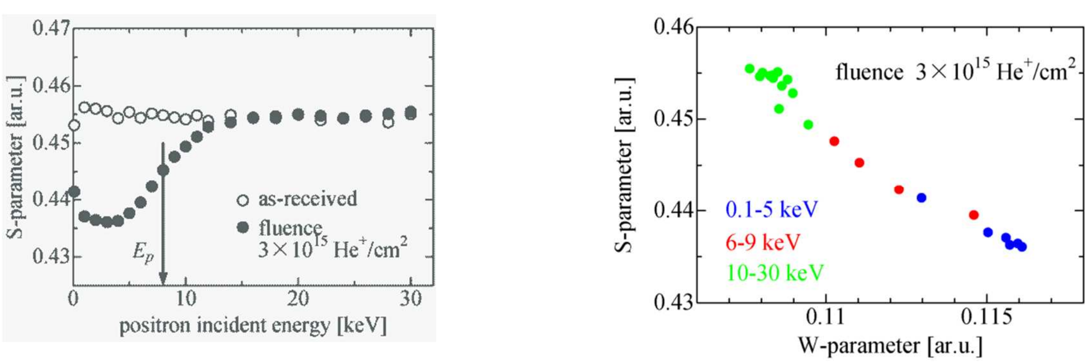


Figure 3 Solid circles indicate positron annihilation Doppler broadening S-parameter for the sample irradiated to a fluence of 3×10^{15} He^+/cm^2 as a function of positron energy. A vertical arrow indicates E_p for the middle point of S-parameter. Blank circles indicate S-parameter for an as-received sample.

Figure 4. SW plot for the sample irradiated to a fluence of 3×10[15] He^+/cm^2. Ordinate shows S-parameter and abscissa shows W-parameter. Colour of dots indicates three gropes of positron incident energy.

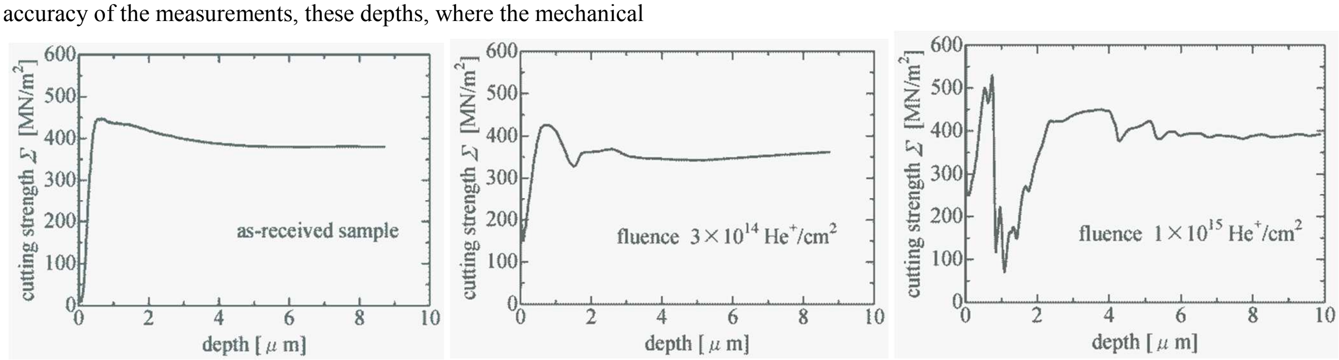
Discussion

In order to investigate the effect of the ion irradiation on the mechanical property, cutting strength , Σ, defined as

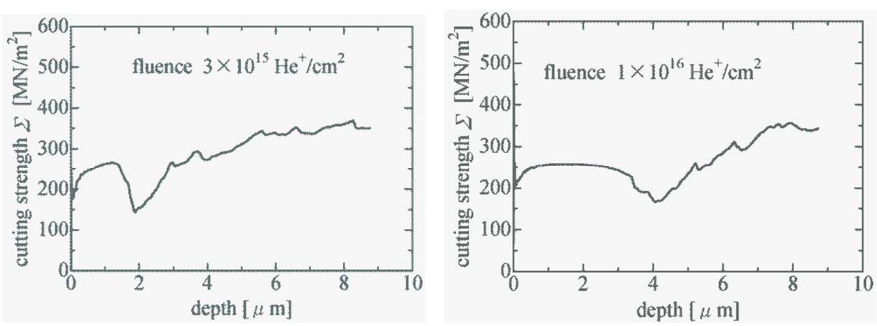
$$\Sigma = \frac{\sqrt{F_h^2+F_v^2}}{bd}, \qquad (1)$$

was deduced from F_h and F_v where b is the width of the cut and d is the depth [10]. The obtained values of Σ are shown in figure 5 as a function of depth. The value of Σ for the as-received sample is nearly constant, ~380 MN/m^2, whereas those for the irradiated samples deviate from constancy and have a minimum as shown in figure 5(b)-(e). The cutting strength Σ for the sample irradiated to the fluences of 3 ×10^{14} He^+/cm^2 and 1 ×10^{15} He^+/cm^2 show minima around 1.6 μm and 1.1 μm, respectively. Within the limits of the accuracy of the measurements, these depths, where the mechanical strength is lowest, are nearly the same position of the Bragg peak around 1.3 μm simulated by TRIM code; figure 6 shows the distribution of He^+ ions with energy of 150 keV in PLLA estimated by the TRIM code. This indicates that nuclear energy loss is responsible for a heavy damage and thus it is possible to estimate the average projected range from the position of the minimum in Σ. The average projected range increased significantly with fluence, up to ~4 μm for the fluence of 1 ×10^{16} He^+/cm^2.

The value of the strength Σ for the depth smaller than that for the minimum is larger than that for the larger depth for the fuluences equal to or less than 3×10^{14} He^+/cm^2 (figure 5(b) and (c)), while an opposite is seen for the fuluences larger than 3×10^{14} He^+/cm^2 ((d) and (e)). This is interpreted as that the formation of crosslinking is dominant for low fluence, whereas cleaving of molecular bond becomes dominant with increasing fluence.



(a) (b) (c)



(d) (e)

Figure 5 Cutting strength, Σ, as a function of depth; (a) as-received, (b) with a fluence of 3×10^{14} He^+/cm^2, (c) 1×10^{15} He^+/cm^2, (d) 3×10^{15} He^+/cm^2, and (e) 1×10^{16} He^+/cm^2.

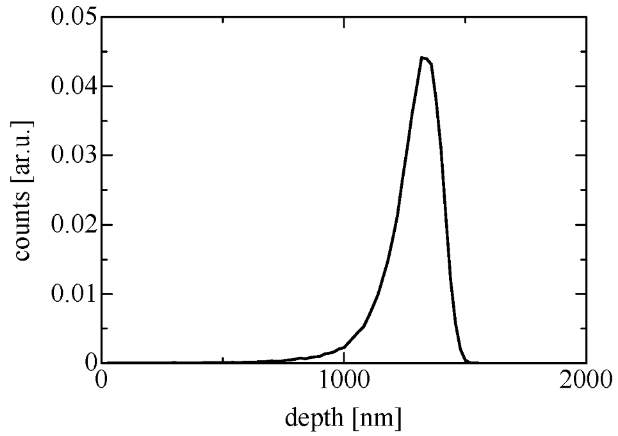


Figure 6 Simulated distribution of He^+ ion with energy 150 keV in PLLA

The increase in the projected range observed is attributed to the decrease in the density of the irradiated part as is the case for the irradiation with high energy ions [4, 5, 6]. Since the positron is much lighter than ions, it does not damage the sample during the measurements. The average positron implanted depth $z(E_\mathrm{p})$ increases with implantation energy E_p as

$$z(E_\mathrm{p}) = 0.04\frac{(E_\mathrm{p}/\mathrm{keV})^{1.6}}{\rho/(\mathrm{g}/_{\mathrm{cm}^3})}\ \mu\mathrm{m}, \qquad (2)$$

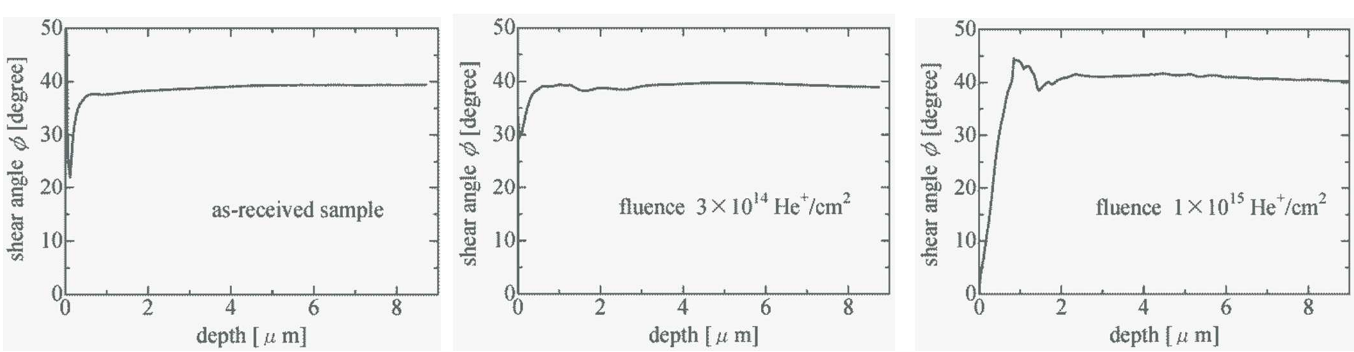
where ρ is the density of the target material [12]. If $z(E_\mathrm{p})$ corresponding to E_p is determined by an independent method, it is possible to estimate the target density as

$$\rho/(\mathrm{g}/_{cm^3}) = 0.04\frac{\left(E_\mathrm{p}/_{\mathrm{keV}}\right)^{1.6}}{z(E_\mathrm{p})/_{\mu\mathrm{m}}}. \qquad (3)$$

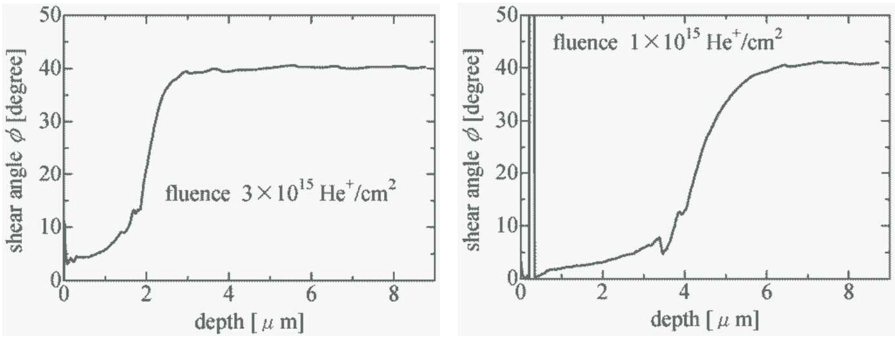
For the sample irradiated to a fluence of 3×10^{15} He^+/cm^2, the positron implantation energy E_p with which the positron penetration depth is equal to the depth of the Bragg peak is about 8 keV as discussed in the previous section. The actual depth of the Bragg peak, $z(E_\mathrm{p})$, itself is known from the measurements of cutting resistance to be 2 μm. Substituting these values to equation (3), the density of the irradiated region was estimated to be ~0.6 g/cm^3.

Using the obtained density as well as the subsidence measured by AFM, the loss of the weight during the irradiation was estimated as follows. We assume that the surfaces of the samples irradiated with a mask plate of a wide opening are nearly flat as a whole except near the edges as seen in the sample irradiated with a mask plate of a slit 0.2 mm wide. The subsided region 1.3 μm deep lost all of its weight. In addition, the region with the depth of 2 μm lost 53 % of the weight, since the density was changed from 1.27 g/cm^3 to 0.6 g/cm^3. Thus, the loss of the weight in the irradiated region consisting of the depression of 1.3 μm and the region of 2 μm with reduced density is about 70 % of its initial weight.

Comparison of the behaviour of the perpendicular component of the cutting resistance, F_v, with that of the horizontal component, F_h, for the samples with the fluence above 3×10^{15} He^+/cm^2 gives some more information on the mechanical property of the irradiated region. For the samples with the fluence below 1×10^{15} He^+/cm^2, the value of F_h is larger than that of F_v, whereas the latter becomes larger than the former in the ion-irradiated region for the samples with the fluence above 3×10^{15} He^+/cm^2. This suggests that mechanical strength in the direction normal to the surface became higher than that in the lateral direction. The formation of the anisotropic mechanical property also evidenced by the change in shear angle, ϕ, deduced from the cutting resistance presuming that the sample is uniform and isotropic [13, 14, 15]. The shear angle, ϕ, for the samples with the fluence above 3×10^{15} He^+/cm^2 are below 10° as shown in figure 7 (d) and (e), while it is usually about 45° for uniform and isotropic materials as seen in figure 7 (a) – (c).



(a) (b) (c)



(d) (e)

Figure 7 Shear angle, ϕ is shown as a function of depth; (a) for the sample as-received, (b) for the sample with a fluence of 3×10^{14} He^+/cm^2, (c) 1×10^{15} He^+/cm^2, (d) 3×10^{15} He^+/cm^2, and (e) 1×10^{16} He^+/cm^2.

The formation of the anisotropic structure probably means that the region which was damaged by scission of molecular chains and deprived of the volatile species was reconstructed with the crosslinks perpendicular to the surface during the following irradiation.

Conclusions

Effects of the irradiation of 150 keV He^+ ions to fluences from 3×10^{14} He^+/cm^2 to 1×10^{16} He^+/cm^2 on the mechanical properties of poly-L-lactic acid (PLLA) was studied. The ion irradiation caused scission of molecular chains of the sample and emission of volatile products from the surface. Cutting strength deduced from the cutting resistance showed that the average projected range of the ions increased, as the fluence increased, from about 1.6 μm for a fluence of 3×10^{14} He^+/cm^2 to about 4μm for a fluence of 1×10^{16} He^+/cm^2. This is explained by the decrease in the density of the irradiated part. The change in the density was obtained qualitatively from 1.27 g/cm^3 for the as received sample to ~0.6 g/cm^3 for the sample irradiated to a fluence of 3×10^{15} He^+/cm^2. It was also observed that the surface of the irradiated sample subsided and the amount of the subsidence increased with fluence. Judging from the decrease in the density and the subsidence of the surface, the part irradiated to the fluence of 3×10^{15} He^+/cm^2 lost 70% of its weight.

Notes and references

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