Effect of argon ion-implantation on mechanical and degradation properties of bulk-shaped poly(lactic acid)

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Abstract
Poly(lactic acid) (PLA) has attracted much attention as a material for bioabsorbable bone fixation devices, however degradation rate of PLA is very low. Surface treatment of PLA has been investigated to increase degradation rate due to improvement in hydrophilicity. In this study, effects of ion-implantation on degradation rate and mechanical properties were investigated. Argon gas which is chemically stable was used as ion source, and argon ion was implanted in the surface of PLA. The contact angle and the surface roughness of the ion-implanted PLA were measured to evaluate hydrophilicity, and tensile tests and micro-indentation tests were conducted to evaluate mechanical properties. The difference in surface morphology after in vitro degradation test between ion-implanted and un-implanted region was observed to investigate degradation properties of ion-implanted PLA. As a result, tensile strength increased by 8.2 % compared to un-implanted specimen and Vickers hardness increased by 9.5%. The ion-implantation might affect mechanical properties in the overall specimen rather than those in the surface. The result of in vitro degradation test showed that an initial degradation rate was accelerated by ion-implantation. This result is consistent with the increasing hydrophilicity of ion-implanted PLA. Those results suggested that ion-implantation accelerates degradation of PLA without decreasing mechanical properties.

Keywords: Poly(lactic acid), Bioabsorbable, Ion-implantation, Degradation rate, Mechanical properties

1. Introduction

Poly(lactic acid) (PLA) has been attracting much attention as material of bioabsorbable bone fixation devices, since PLA bio-degrades in living body and a product of the decomposition is nontoxic. However, degradation rate of PLA is very slow, and it was reported that PLA devices were remained after an implantation period of over 5 years in the treatment of bone fracture (Bergama, et al., 1995). Copolymer of PLA and poly(glycolic acid) (PLGA) (Jan, et al., 2005, Rokkanen, et al., 1985, Böstman, et al., 1990) and/or copolymer of poly(L-lactide) and poly(D-lactide) (PDLLA) (Majola, et al., 1992, Prokop, et al., 2005) which have high degradation rate were investigated to improve degradation rate of PLA. However, Prokop et al. reported that degradation period of PDLLA is 3 years which is longer than bone fracture healing period of about 24 weeks (Prokop, et al., 2005). Surface treatment of PLA has been investigated to increase degradation rate due to improvement in hydrophilicity. Zhang et al. reported that the surface hydrophilicity of the PLA was improved by electron beam irradiation (Zhang, et al., 2010). The improvement in hydrophilicity might be due to increase hydrophilic groups which was occured by chain scission induced by electron beam irradiation. Wang et al. reported that the surface hydrophilicity of the poly-ether-ether-ketone (PEEK) was improved by ion-implantation. It is explanted that the cause of this hydrophilicity improvement was construct hydroxyl groups as well as ravine structure, which increase specific surface area (Wang, et al., 2014). Moreover, surface properties can be adapted by
selecting of ion source (Colwell, et al., 2003).

The purpose of this study is to investigate the effect of ion-implantation on mechanical and degradation properties of PLA. Before investigation of effect of ion source on mechanical and degradation properties, effect of surface properties was investigated in this study. Therefore, argon gas which is chemically stable was used as ion source. The contact angle and the surface roughness of the ion-implanted PLA were measured to evaluate hydrophilicity, and tensile test and micro-indentation test were conducted to evaluate mechanical properties. The difference in surface morphology after in vitro degradation test between ion-implanted and un-implanted region was observed to investigate degradation properties of ion-implanted PLA.

2. Experiments
2.1 Preparation of Specimen

Commercially-available PLA pellets (Ingeo 3001D, Nature Works LLC, the USA) were used as a material of specimens in this study. The PLA pellets have number average molecular weight of about 87,000, weight average molecular weight of about 155,000, glass-transition temperature of about 73 °C and melting point of 170 °C. The dumbbell specimen which has parallel portion length of 30 mm, width of 5 mm and thickness of 2 mm was injection molded from this pellets using a small-size injection molding machine (NP7 Real Mini, Nissei Plastic Industrial Co., LTD.). The injection conditions were shown as Table 1.

Ion-implanted specimen is classified two types according to implanted region. The one specimen was ion-implanted on half-surface of one side as shown in Fig. 1. The other specimen was ion-implanted on the whole surface of both sides. Argon was used as ion source, and the argon ion was implanted at acceleration energy of 50, 100, 150 keV and dose of $10^{13}$, $10^{14}$, $10^{15}$ ion/cm$^2$.

| Table 1 Condition of injection molding. |
|-----------------------------------------|
| Injection Pressure | 82 MPa |
| Fusion Temperature | 200 °C |
| Clamping Temperature | 50 °C |
| Cooling Time | 30 s |

2.2 Surface Characterizations

The contact angle and the surface roughness were measured to examine surface properties of ion-implanted specimen. The contact angle was measurement by sessile drop method using contact angle measurement (DM301, Kyowa Interface Science Co., LTD.). The purified water of about 10 μl was dropped on specimen. After 1 s, the contact angle was measured. The surface roughness was examined by atomic force microscopy (AFM; Dimension Icon, Bruker BioSpin K. K.). The AFM was operated in tapping mode on a scanning area of 60 μm×60 μm, and the root mean square deviation roughness of the specimen was estimated.

2.3 Tensile Test

The tensile tests were conducted to investigate mechanical properties for ion-implanted specimens. The specimens which were ion-implanted on both surfaces were used in the tensile tests. The tensile tests were conducted by using a universal testing machine (AGS-1000A, Shimadzu) operated at a cross head speed of 0.5 mm/min in atmosphere and room temperature.

2.4 Micro-indentation Test

The mechanical property in ion-implanted surface region was investigated by micro-indentation. The specimens half surface of which were ion-implanted as shown in Fig. 1 were used. The indentation test was conducted by using a...
dynamic ultra-micro hardness tester (DUH-211, Shimadzu) on ion-implanted region and un-implanted region. The specimen was indented by using a Vickers indenter with loading of 5 gf for 5 s. Vickers hardness was calculated from diagonal length of indentation.

2.5 In vitro Degradation for Ion-implanted Specimen

The degradation property for ion-implanted specimen was investigated by comparing the difference in surface morphologies after in vitro degradation test between ion-implanted and un-implanted region. The specimens half surface of which were ion-implanted were immersed in phosphate buffered solution (PBS) at pH 7.4 and 37 °C. PBS was prepared with phosphate buffered powder (Wako Pure Chemical Industries) to concentration of 1/15 mol/l in pure water. The specimen was immersed for 0, 1, 2, 4 and 6 weeks. PBS was changed weekly to avoid the effect of acidic product of decomposition from the specimen. After in vitro degradation test, the difference between ion-implanted and un-implanted region as shown in Fig. 2 was measured by using AFM. The AFM was operated in tapping mode on a scanning area of 60 μm×60 μm.

Un-implanted Area Ion-implanted Area

Phosphate Buffered Solution

Figure 2 Definition of the difference generated during immersion.

3. Result

3.1 Measurement of Contact Angle

Figure 3 shows the variation in contact angle for ion-implanted specimen in each acceleration energies and the dose of $10^{13}$ ion/cm$^2$. Figure 4 shows the variation in contact angle on ion-implanted specimen in each doses and the acceleration energy of 100 keV. The leftmost plot on those graphs shows contact angle on un-implanted specimen. Those results showed that contact angle decreased from about 74° to 61° with increasing dose and acceleration energy.

![Figure 3 The variation of contact angle in acceleration energy.](image)

![Figure 4 The variation of contact angle in dose.](image)
3.2 Measurement of Surface Roughness

Figure 5 showed the variation in surface roughness on ion-implanted specimen in each acceleration energies and the dose of $10^{13}$ ion/cm$^2$. There was no significant difference in the surface roughness of ion-implanted and un-implanted specimen.

![Figure 5 Dependence of surface roughness in acceleration energy.](image)

3.3 Tensile Test

The stress-cross head displacement curves during tensile tests were shown in Fig. 6. Each curve is offset by 0.1 mm to allow comparison. Tensile strengths for ion-implanted specimens were shown in Fig. 7. There was no significant difference in the slopes of the curves in Fig. 6. On the other hands, total elongation decreased with increasing acceleration energy and dose. The p-values between tensile strengths of un-implanted and ion-implanted specimen shown in Fig. 7 were calculated, and compared to significance level of 0.05. As a result, the significant difference was observed the highest acceleration energy of 150 keV and dose of $10^{15}$ ion/cm$^2$ as shown in Table 2. Hence, tensile strength increased with acceleration energy and ion dose as shown in Fig. 7. The maximum tensile strength is higher by 8.2% than that of un-implanted specimen.

![Figure 6 Tensile stress and cross-head displacement curve during tensile test.](image)

![Figure 7 Tensile strength of ion-implanted specimen.](image)

Table 2 The p-values between tensile strengths of un-implanted and ion-implanted specimen.

| Acceleration Energy [keV] | Dose $[10^x$ ion/cm$^2$] | p-Value |
|--------------------------|--------------------------|---------|
| Un-implantation          | Un-implantation          | -       |
| 50                       | 13                       | 0.1639  |
|                          | 15                       | 0.5529  |
| 150                      | 13                       | 0.2315  |
|                          | 15                       | 0.0083  |
3.4 Micro-indentation Test

Vickers hardness in ion-implanted and un-implanted areas was shown in Fig. 8 (a) and (b). The p-values between Vickers hardness of specimens shown in Fig. 8(b) which have conditions of ion-implantation (50 keV, 10^{13} ion/cm^2) and other conditions were calculated, and compared to significance level of 0.05. As a result, the significant difference was observed the highest acceleration energy of 150 keV and dose of 10^{15} ion/cm^2 as shown in Table 3. Hence, Vickers hardness in ion-implanted area increased with acceleration energy and dose. The highest Vickers hardness is higher by 9.5% than that for un-implanted area. Indentations in ion-implanted and un-implanted areas on specimen which ion-implanted for acceleration energy of 150 keV and dose of 10^{15} ion/cm^2 were shown in Fig. 9 (a) and (b). Fig. 9 (b) showed that indentations in ion-implanted area are unclear.

![Figure 8 Vickers hardness for each implantation condition.](image1)

Table 3 The p-values between Vickers hardness of specimens which have conditions of ion-implantation (50 keV, 10^{13} ion/cm^2) and other conditions.

| Acceleration Energy [keV] | Dose [10^14 ion/cm^2] | p-Value |
|--------------------------|------------------------|---------|
|                          | 13                     | -       |
| 50                       | 14                     | 0.6048  |
|                          | 15                     | 0.9277  |
| 100                      | 13                     | 0.7855  |
|                          | 14                     | 0.6422  |
|                          | 15                     | 0.0551  |
| 150                      | 13                     | 0.0588  |
|                          | 14                     | 0.3559  |
|                          | 15                     | 0.0325  |

![Figure 9 Indentations on the specimen acceleration energy of 150 keV and dose of 10^{15} ion/cm^2.](image2)
3.5 In vitro Degradation for Ion-implanted Specimen

Figures 10 and 11 show the difference in degradation depth between ion-implanted and un-implanted region after in vitro degradation tests. Figures 10 and 11 also show the effect of acceleration energy and ion dose on the variation in difference during immersion in PBS, respectively. Those results show that the difference after immersion increased with acceleration energy, dose and immersion times. This difference in degradation depth during immersion saturated at about 6 weeks.

The comparison of roughness on ion-implanted and un-implanted region during immersion was shown in Fig. 12. The roughness of both specimens increased with immersion time. The increment of roughness during immersion increased by ion-implantation.

4. Discussion

Argon gas was used as ion source. The argon ion in specimen might volatilize after ion-implantation, because of chemical stability of argon. However, contact angle as shown Fig. 3 and 4 was decreased by implantation of argon ion. Furthermore, indentations in un-implanted and ion-implanted area as shown Fig. 9 were clearly different, and increment of roughness during immersion increased by ion-implantation as shown Fig. 12. Those results suggested that argon ion was implanted in specimen.

4.1 Hydrophilicity of Ion-implanted Specimen

The results for Fig. 3 and 4 showed that contact angle decreases with increasing acceleration energy and dose during ion-implantation. This might be due to molecular chains scission on the surface of specimen caused by ion-implantation. This chain scission increases the end hydroxyl groups which results in increasing hydrophilicity of
PLA. The contact angle on PLA surface decreased from about 74° to 61° by ion-implantation. Minoura et al. (Minoura, et al., 1985) reported that the initial cell attachment became highest in the range of contact angle 60 - 70°. Hence, the ion-implantation might improve the cell attachment on surface of PLA.

The result for Fig. 5 showed that there is no significant difference in the surface roughness of ion-implanted and un-implanted specimen. This result shows that ion-implantation has not varied in surface morphology. Hence, the improvement in hydrophilicity caused by ion-implantation might be caused by the decrease in contact angle rather than the variation in surface morphology.

4.2 Mechanical Properties of Ion-implanted Specimen

The result of Fig. 7 showed that ion-implantation improves tensile strength by 8.2 %. This increasing tensile strength for ion-implantation might be due to the change in properties on specimen surface. Therefore, micro-indentation test was conducted to investigate mechanical properties on the surface region. Vickers hardness increased up to 9.5 % with acceleration energy and dose for ion-implantation. It was reported that mechanical properties of PLA decreased with molecular weights (Gogodewski, et al., 1983). This is inconsistent with trend of tensile strength and Vickers hardness. Fig. 9 (b) showed that indentations in ion-implanted area are unclear. This might be due to viscoelastic recovery around the indentation in ion-implanted specimen. Hence, apparent Vickers hardness increased by viscoelastic recovery of indentations.

Next, indentation depth and theoretical ion-implantation depth were compared in Table 4 to discuss the effect of ion-implanted region on tensile strength and Vickers hardness. Theoretical ion-implantation depth was calculated by binary collision approximation using Stopping/Range Tables in SRIM 2008 as a solver. Ar ion was accelerated with the energies of 50 keV, 100 keV and 150 keV and was implanted into the matrix with the density of 1.24 g/cm³. From the analysis, the maximum ion-implanted depth in acceleration energy of 150 keV is about 240 nm. This implanted depth corresponded to 0.024 % of total thickness and occupied 18.6 % of indentation depth, whereas the increase in tensile strength and Vickers hardness by ion-implantation is 8.2 % and 9.5 %, respectively. Hence, the mechanical properties in overall specimen might depend on ion-implantation rather than that of surface region.

Next, the slopes of stress-displacement curves did not indicate any significant change in Fig. 6. This may be due to the fact that the elastic modulus is insensitive to the structure. The slopes of stress-displacement curves correspond with the elastic modulus. This elastic modulus might be not affect of change in surface properties by ion-implantation because the elastic modulus is insensitive to the structure. On the other hands, total elongation remarkably decreased by ion-implantation. This might be due to decrease toughness with molecular weight. It was reported that the toughness of polymer decreased with molecular weight (Notomi et al., 1999). Hence, ion-implantation decreased molecular weight on specimen surface, and decreased the toughness. As a result, total elongation might have decreased.

Table 4 The comparison of ion implantation depth and indentation depth.

| Acceleration Energy [keV] | Indentation Depth [µm] | Ion-implantation Depth [nm] | Depth Ratio [%] |
|---------------------------|------------------------|-----------------------------|-----------------|
| 50                        | 3.39                   | 80 ± 20                     | 6.91            |
| 100                       | 3.41                   | 160 ± 30                    | 13.4            |
| 150                       | 3.46                   | 230 ± 40                    | 18.6            |

4.3 Degradation Properties of Ion-implanted Specimen

The results of Figs. 10 and 11 showed that the difference after immersion increased with acceleration energy and dose. This might be due to increasing degradation rate by ion-implantation. Molecular chains in surface region were cut off by ion-implantation, and this chain scission increased the hydrophilic end groups in PLA. The hydrophilicity increased degradation rate since the degradation mechanism for PLA mainly consists of hydrolysis caused by water molecules. The hydrophilicity increased with dose as shown in Fig. 4, and ion-implantation depth increased with acceleration energy as shown in Table 2. Hence, degradation rate increased with acceleration energy and dose.

The increase in the difference in degradation depth during immersion saturated up to about 6 weeks. This result suggested that increasing degradation rate by ion-implantation is limited around surface region. The degradation rate
and dissolution of degradation products in ion-implanted layer was faster than the diffusion rate of water molecules in un-implanted region. Ion-implanted layer which has higher hydrophilicity eluted before water molecules diffuses in un-implanted region. Therefore, degradation rate went back to the same rate before ion-implantation.

The result of Fig. 12 showed that increment of roughness during immersion increased by ion-implantation. This might be due to increasing degradation rate cause by ion-implantation. This increasing roughness is associated with increasing specific surface and is considered to accelerate degradation rate at the later stage of immersion.

5. Conclusion

In order to investigate the effect of ion-implantation on mechanical and degradation properties of PLA, contact angle, tensile strength, surface hardness and difference in degradation height were measured for ion-implanted or un-implanted injection molded PLA. As a result, hydrophilicity of ion-implanted PLA was improved. The improvement in hydrophilicity was dominated by the decrease in contact angle rather than the surface morphology. The decrease in contact angle might be due to the scission of the molecular chains caused by ion-implantation.

The results of tensile test and micro-indentation showed that tensile strength increased by only 8.2 % compared to un-implanted specimen and Vickers hardness increased by 9.5%. Those results might suggest that the ion-implantation affects mechanical properties in overall specimen rather than surface. The result of in vitro degradation test showed that initial degradation rate was improved by ion-implantation.

Those results showed that ion-implantation accelerates degradation of PLA without decreasing mechanical properties, and might improve the cell attachment on surface of PLA; because contact angle of ion-implanted PLA was 60 -70° which angle has highest cell attachment (Minoura, et al., 1985).

References

Bergsma, J., E. Bruijn, W. C. Rozema, F. R. Bos, R. M and Boering, G., Late degradation tissue response to poly(l-lactide) bone plates and screws, Biomaterials, Vol. 16, (1995), pp.25-31.

Böstman, O. Hirvensalo, E. Mäkinen, J. and Rokkanen, P., Foreign-body reactions to fracture fixation implants of biodegradable synthetic polymers, The Journal of bone and joint surgery. British volume, Vol. 72, (1990), pp.592-596.

Colwell, J. M. Wentrup-Byrne, E. Bell, J. M. and Wielunski, L. S., A study of the chemical and physical effect of ion implantation of microporous and nonporous PTFE, Surf. Cott. Technol., Vol. 168, (2003), pp.216-222.

Gogolewski, S. and Pennings, A. J., Resorbable Materials of Poly(L-Lactide). II. Fibers Spun from Solutions of Poly(L-Lactide) in Good Solvents, Journal of Applied Polymer Science, Vol. 28, (1983), pp.1045-1061.

Jan, C. and Grzegorz, K., The study of lifetime of polymer and composite bone joint screws under cyclical loads and in vitro conditions, Journal of materials science. Materials in medicine, Vol. 16, (2005), pp.1051-1060.

Majola, A. Vainionpää, S. Rokkanen, P. Mikkola, H. M. and Törmälä, P., Absorbable self-reinforced polylactide (SR-PLA) composite rods for fracture fixation: strength and strength retention in the bone and subcutaneous tissue of rabbits, Journal of Materials Science: Materials in Medicine, Vol. 3, (1992), pp.43-47.

Minoura, N. Aiba, S. Fujiwara, Y. Yamada, S. Watanabe, A. and Imai, Y., Interaction between poly(α-amino acid) membranes and cell, The Chemical Society of Japan, Vol. 6, (1985), pp.1252-1258 (in Japanese).

M. Notomi, H. Inaba, K. Kishimoto, T. Shibuya, A. Morita, Y. Yoshida. The Effect of Molecular Weight on Tensile Property and Fracture Toughness of the Polyimide Resin, Transactions of the Japan Society of Mechanical Engineers, A, Vol. 65, pp. 67 - 71, 1999 (in Japanese).

Prokop, A. Jubel, A. Hahn, U. Dietershagen, M. Bleidistel, M. Peters, C. Höfl, A. and Rehm, K. E., A comparative radiological assessment of polylactide pins over 3 years in vivo, Biomaterials, Vol. 26, (2005), pp.4129-4138.

Rokkanen, P. Vainionpää, S. Törmälä, P. Kilpihari, J. Böstman, O. Vihonen, K. Laiho, J. and Tamminnäki, M., Biodegradable implants in fracture fixation: early results of treatment of fractures of the ankle, The Lancet, Vol. 325, (1985), pp.1422-1424.

Wang, H. Lu, T. Meng, F. Zhu, H. and Liu, X., Enhanced osteoblast responses to poly ether ether ketone surface modified by water plasma immersion ion implantation, Colloids and Surfaces B: Biointerfaces, Vol. 117, (2014), pp.89-97.
Zhang, X. Kotaki, M. Okubayashi, S. and Sukigara, S., Effect of electron beam irradiation on the structure and properties of electrospun PLLA and PLLA/PDLA blend nanofibers, Acta Biomaterialia, Vol. 6, (2010), pp.123-129.