Transactions of the Materials Research Society of Japan 28 [2] 503-506 (2003)

Surface Analysis of Ion-Beam Irradiated poly-$_L$-Lactic Acid

Tasuku Yotoriyama, Yoshiaki Suzuki*, Masaya Iwaki* and Takeyo Tsukamoto

Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan
Fax: 81-03- 3260-4772, e-mail: yotoriya@postman.riken.go.jp
*RIKEN, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan
Fax: 81-048-462-4623

An ion-beam was irradiated into biodegradable polymer sheets to develop thin-film, self-assembled cellular sheets that exfoliated spontaneously from the substrate in a water solution. The substrates used were Poly-$_L$-lactic Acid (PLLA) sheets. He^+, Ne^+, Ar^+ and Kr^+ ion-beam irradiation was performed at an energy of 150 keV with fluences between 1×10^{13} and 1×10^{15} ions/cm^2. FT-IR-ATR study indicated that the He^+ ion-beam irradiated surface produced new peaks at 3400 and 1620 cm^{-1} due to hydroxyl (O-H) and C=C double bonds. This tendency appeared with an increase in ion fluences. The formation of new carbon structures is induced by Ar^+ and Kr^+ ion-beam-irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2. The maximum contact angle of water dropped on Ar^+ ion-beam irradiated PLLA with a fluence of 1×10^{15} ions/cm^2 increased from an initial angle of 73° to 83° owing to the new carbon structure. We conclude that ion-beam irradiation produced new functional groups and carbon structures as a function of ion species and fluences in combination with the electronic stopping powers and the nuclear stopping powers.

Key words: Self-assembled cellular sheet, Raman, FT-IR-ATR, Wettability

1. INTRODUCTION

Bombardment with energetic ions is a unique method of modifying surface structures and properties of materials. Most research efforts in the field of ion-beam irradiation have concentrated on such inorganic materials as metals, ceramics and semiconductors. In recent years, ion-beam irradiation into polymers was investigated and ion-beam irradiation has been applied to modify the surfaces of polymers to improve their compatibility with blood and tissue [1-3]. However, biomedical polymers using local energy deposition induced by ion-beam irradiation have not been investigated. Our previous study reported that ion-beam irradiation into a biodegradable polymer produced a thin-film, self-assembly cellular sheet or spheroid, which exfoliated spontaneously from the substrate in a water solution [4]. The purpose of the present work is to characterize the ion-beam-irradiated PLLA surfaces and to investigate the exfoliation mechanisms using Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy combined with attenuated total reflectance (FT-IR-ATR), Raman scattering measurement, and contact angle measurement.

2. EXPERIMENTAL

The substrates used were Poly-$_L$-lactic acid (PLLA) sheets (LACTY; SHIMADZU, Co., Kyoto, Japan) fabricated on 3 cm × 3 cm substrates. The atomic density of PLLA was 1.27 g/cm^3 and the thickness of the sheet was 200 μm. PLLA is a biodegradable polymer; when implanted in a body, it hydrolyzes into a low molecule. The hydrolysis-generated reaction products are non-toxic to the body since they are decomposed into carbon dioxide and water by the body's metabolism cycle.

He^+, Ne^+, Ar^+ and Kr^+ ion-beam irradiation was performed at an energy of 150 keV with fluences of 1×10^{13}, 1×10^{14} and 1×10^{15} ions/cm^2 at room temperature using the RIKEN 200 kV Low Current Implanter. The beam-current density was kept below 0.1 μA/cm^2 to prevent increasing the specimen temperature, and the pressure in the target chamber was 6.0×10^{-4} Pa..

SEM observation (JSM-6330F : JEOL) was used to investigate a cross section obtained by cutting the ion-beam-irradiated PLLA fixed by epoxy resin, and the thickness of the thin film was measured.

We performed cell culturing on ion-beam-irradiated surfaces before exfoliation from the base material. Bovine aorta endothelial cells (BAECs) were used. BAECs were suspended in a culture medium (RPMI 1640; Nissui Pharm., Co., Japan) supplemented with 10% fetal bovine serum (FBS; CCS SO7200, Sanko Junyaku Co., Japan). We initially seeded cells at 2.5×10^4 cells/ml then incubated the cells at 37°C in a humidified atmosphere with 5% CO_2. The extent of cell attachment and spreading was determined visually with an optical microscope equipped with phase contrast objectives and a CCD camera (IX-50; Olympus Co., Tokyo, Japan).

The electronic and nuclear stopping powers were calculated by means of the SRIM code (IBM, Co., USA), which included the theory of Linhard et al. (LSS) [5]. The stopping powers were calculated for a density of 1.27 g/cm^3 and a composition element ratio of C: H: O = 3: 4: 2.

Functional group analyses for irradiated PLLA were carried out by means of FT-IR-ATR (Nexus 470, Thermo Nicolet, USA). In these analyses, the incident angle of light emitted from ceramic Ge on the samples was 45°, and the absorbance was obtained as a function of wavenumber by measuring the intensity of the reflected light. Each spectrum was obtained after at least 128 scans and averaged at a resolution of 4 cm^{-1} from 4000 to 400 cm^{-1}.

Raman scattering measurements were performed at room temperature with a 632.817 nm He-Ne laser. The spectra were recorded by a Jobin Yvon LABRAM with a photo-multiplier and photon-counting electronics.

Wettability immediately after irradiation was investigated by measuring the contact angles of water dropped on the surfaces of the irradiated samples, that is a sessile drop method of water.

3. RESULTS AND DISCUSSION

3.1 SEM Observation

Figure 1 shows a cross-sectional SEM photograph of He^+ ion-beam-irradiated specimen at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2 fixed by epoxy resin. It was clarified that a space exists in the substratum by ion beam irradiation. He^+ ion-beam irradiation formed a thin film at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2 and its thickness was about 1200 nm.

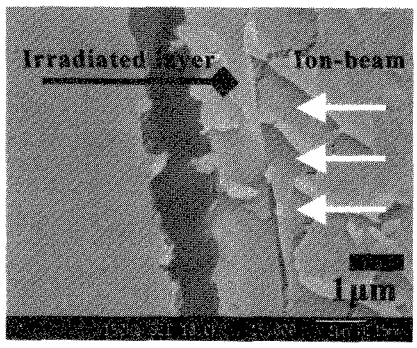

Fig.1 Cross sectional SEM photograph of He^+ ion-beam irradiated layer at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2.

3.2 Cell Attachment

Figure 2 shows cell attachment to a He^+ ion-beam-irradiated linear domain with a width of 140 μm at a energy of 150 keV with a fluence of 1×10^{15} ions/cm^2 after an incubation of 24 h. The seeded cells recognized the surface of the ion-beam irradiated PLLA and selectively attached to the ion-beam-irradiated domain.

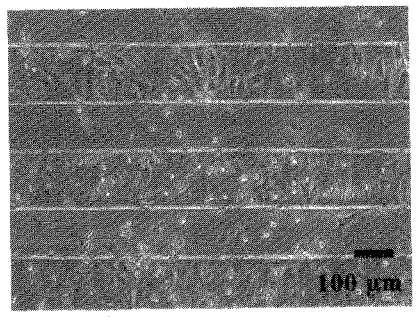

Fig.2 Phase-contrast photograph of BAECs attachment to He^+ ion-beam-irradiated patterning domain of PLLA at 150 keV, 1×10^{15} ions/cm^2 after an incubation of 24 h.

3.3 Stopping Powers

Figure 3 shows the electronic stopping power (A) and nuclear stopping power (B) of He^+, Ne^+, Ar^+ and Kr^+ irradiated ions as a function of energy. The energy deposited by light ions like He^+ is almost completely dissipated via electronic losses, and relatively few nuclear collisions occur. Heavier species, however, show both appreciable electronic and nuclear collisions events. The nuclear stopping powers are directly related to the displacement of atoms in the sample and effects on physical structures. The electronic stopping powers are related to the energy transfer from energetic ions to the electrons surrounding the nuclei in the sample and effects on breakage of bonds. This kind of energy transfer ionizes the atoms in the sample [6].

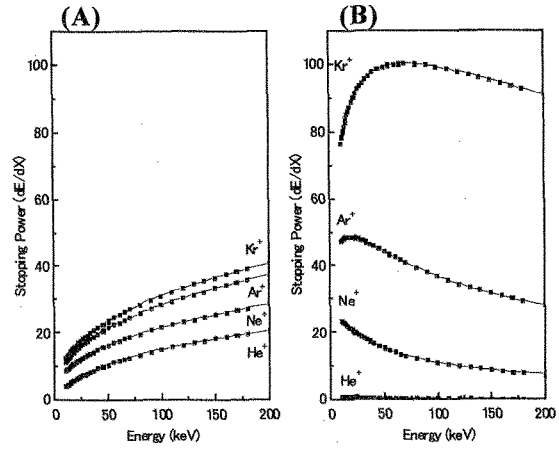

Fig.3 The electronic stopping power (A) and nuclear stopping power (B) of He^+, Ne^+, Ar^+ and Kr^+ irradiated ions as a function of energy.

3.4 FT-IR-ATR Analysis

Figure 4 shows the FT-IR-ATR spectra of non-irradiated PLLA and the He^+ ion-beam-irradiated PLLA at energies of 150 keV with fluences of 1×10^{13}, 1×10^{14} and 1×10^{15} ions/cm^2 (A), Ne^+ ion-beam irradiated (B), Ar^+ ion-beam irradiated (C) and Kr^+ ion-beam irradiated (D). The spectrum of the non-irradiated surface contains three main peaks at 1080, 1180 and 1740 cm^{-1} assigned to C-O-C and C-C-O stretching vibration of ether-like, ester-like or carboxylic acid functionalities (1080 and 1180 cm^{-1}) and C=O stretching vibration (1740 cm^{-1}), respectively [7].

The ion-beam irradiated surface produced new peaks at 1620 and 3400 cm^{-1}. The bands at 3400 and 1620 cm^{-1} are due to hydroxyl (O-H) and C=C double bonds, respectively. This tendency appeared with an increase in ion fluence.

3.5 Raman Spectroscopic Studies

Figure 5-(A) shows the Raman spectra of non-irradiated PLLA, He^+, Ne^+, Ar^+ and Kr^+ ion-beam-irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2 in the region of 1000 to 1800 cm^{-1}. Raman spectra of He^+ and Ne^+ ion-beam-irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2 were no different from non-irradiated PLLA. However, new broad peaks

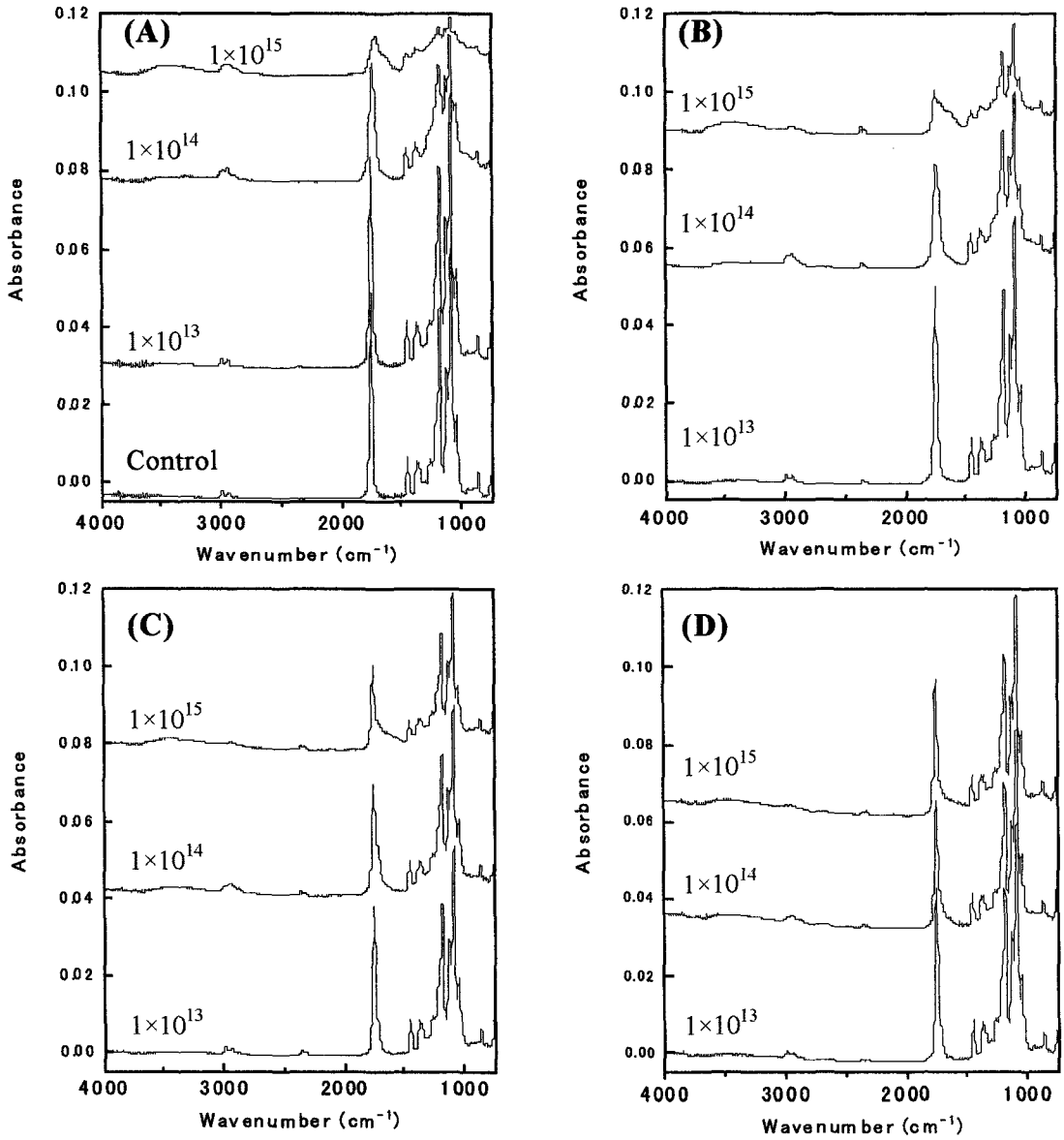

Fig.4 FT-IR-ATR spectra of non-ion-beam-irradiated PLLA and the He^+ ion-beam-irradiated PLLA at an energy of 150 keV with fluences of 1×10^{13}, 1×10^{14} and 1×10^{15} ions/cm^2 (A), Ne^+ ion-beam-irradiated (B), Ar^+ ion-beam-irradiated (C), Kr^+ ion-beam-irradiated (D).

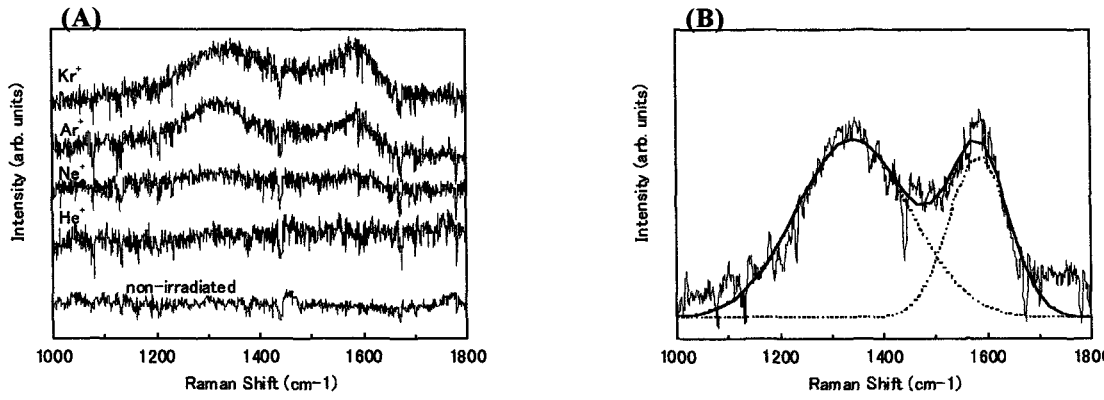

Fig.5 Raman spectra of non-irradiated PLLA, He^+, Ne^+, Ar^+ and Kr^+ ion-beam irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2 in the region of 1000-1800 cm^{-1} (A) and the result of the computer simulation of the differential Raman spectra of Kr^+ ion-beam irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2 (B).

formed between 1000 and 1800 cm^{-1} for Ar^+ and Kr^+ ion-beam-irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2.

Two broad peaks are observed: one centered at 1580 cm^{-1} and the other centered at 1320 cm^{-1}. The higher frequency band is characteristic of polycrystalline graphite (G band) and amorphous carbon with graphitic bonding. The broad lower frequency band is typical of a disordered graphite structure (D band) [8-10].

Heavy ions like Kr^+ were more effective than light ions in producing these two peaks. In order to study the detailed evolution of such peaks, the experimental Raman spectra can be fit into two Gaussian bands centered at about 1320 cm^{-1} and 1580 cm^{-1} by means of a computer simulation. Figure 5-(B) shows the result of the computer simulation of the differential Raman spectra of Kr^+ ion-beam irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2.

The formation of amorphous carbons is proven by the Raman spectra of Ar^+ and Kr^+ ion-beam-irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2. In contrast, amorphous carbons did not form in He^+ and Ne^+ ion-beam-irradiated PLLA.

3.6 Wettability

Figure 6 shows the contact angle of water for non-ion-beam-irradiated and He^+, Ne^+, Ar^+ and Kr^+ ion-beam-irradiated PLLA at an energy of 150 keV with fluences of 1×10^{13}, 1×10^{14} and 1×10^{15} ions/cm^2 immediately after irradiation.

The contact angle of water on non-ion-beam irradiated samples was 73°. The contact angle first increased with a fluence of 1×10^{13} ions/cm^2, then decreased with a fluence of 1×10^{14} ions/cm^2, and finally increased with a fluence of 1×10^{15} ions/cm^2. The maximum value was 84° for Ar^+ ion-beam-irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2.

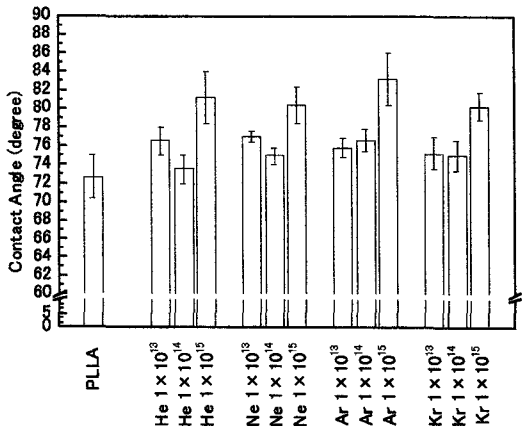

Fig.6 The contact angle of water for non-ion-beam irradiated, He^+, Ne^+, Ar^+ and Kr^+ ion-beam irradiated PLLA at an energy of 150 keV with fluences of 1×10^{13}, 1×10^{14} and 1×10^{15} ions/cm^2 immediately after irradiation.

4. CONCLUSION

We investigated ion-beam-irradiated PLLA by means of FT-IR-ATR, Raman-scattering measurements, and wettability measured by a sessile drop method.

Ion-beam irradiation into PLLA produced decomposition of original chemical bonds and formation of new radicals such as OH and C=C; this tendency was proportional to the mass of irradiated ions.

The formation of polycrystalline graphite (G band), amorphous carbons and disordered graphite structure (D band) is demonstrated by the Raman spectra of Ar^+ and Kr^+ ion-beam-irradiated PLLA at an energy of 150 keV with a fluence of 1×10^{15} ions/cm^2.

The maximum contact angle of water dropped on Ar^+ ion-beam-irradiated PLLA with a fluence of 1×10^{15} ions/cm^2 increased from an initial angle of 73° to 83° owing to the new carbon structure.

He^+ ion-beam irradiation formed the OH radical. However, the carbon structure was primarily due to Kr^+ ion beams.

We clarified that there are two patterns for forming new structures, one caused by the electronic stopping power and the other by the nuclear stopping power.

The electronic stopping powers are related to the energy transfer from energetic ions to the electrons surrounding the nuclei in the sample. This kind of energy transfer due to He^+ ion-beam irradiation ionizes atoms in the sample and forms OH radicals.

The nuclear stopping powers are directly related with the displacement of atoms in the sample. The carbon structure was produced by the nuclear stopping power induced by Kr^+ ion-beam irradiation.

New functional groups and carbon structures were controlled by ion-beam irradiation as a function of ion species and fluences in combination with the electronic stopping powers and the nuclear stopping powers.

REFERENCES

[1] Y. Suzuki, M. Kusakabe, J.-S. Lee, M. Kaibara, M. Iwaki and H. Sasabe, *Nucl. Instrum. Methods Phys. Res.* **B65**, 142-147 (1992).

[2] Y. Suzuki, H. Iwata, A. Nakao, M. Iwaki, H. Sasabe, S. Kaneko, H. Nakajima and M. Kusakabe, *Nucl. Instrum. Methods Phys. Res.* **B127/128**, 1019-1022 (1997).

[3] K. Kurotobi, M. Kaibara, Y. Suzuki, M. Iwaki and H. Nakajima, *Nucl. Instrum. Methods Phys. Res.* **B175/177**, 791-796 (2001).

[4] T. Yotoriyama, Y. Suzuki, T. Tsukamoto and M. Iwaki, *Nucl. Instrum. Methods Phys. Res.* (inpress)

[5] J. Lindhard, M. Scharff and H.F.Sciott, *Kgl. Danske. Videnskab. Selskab. Mat. Fys. Med.*, **33**,14 (1963).

[6] G. Xu, Y. Hibino, Yasuo Suzuki, Yoshiaki Suzuki, K. Kurotobi, M. Osada, M. Iwaki, M. Kibara, M. Tanihara, Y. Imanishi, *Colloids and Surfaces B*: Biointerfaces **19**, 237-247 (2000).

[7] ON. Tretinnikov and Y. Ikada, *J.Polym.Sci., Part B: Polym.Phys.***Vol.36**, 715-725 (1998).

[8] EH Lee, DM Hembree, Jr., GR Rao and LK Mansur, *Phys. Rev. B*, **Vol.**48, 15540 (1993).

[9] Y. Suzuki, M. Kusakabe and M. Iwaki, *Nucl. Instrum. Methods Phys. Res.* **B59/60**, 1300-1303 (1991).

[10] Y. Suzuki, M. Kusakabe and M. Iwaki, *Nucl. Instrum. Methods Phys. Res.* **B91**, 584-587 (1994).

(Received December 21, 2002; Accepted March 26, 2003)