

Surface characterization of chitosan film modified by ion beam

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The surfaces of chitosan film were modified by He⁺, Ar⁺, Kr⁺, N₂⁺ and O₂⁺ beams and were characterized. An ion beam was irradiated at an energy level of 150 keV with fluences of 10¹³, 10¹⁴ and 10¹⁵ ions/cm². The modified surfaces were characterized by Fourier-transform infrared (FT-IR) spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angle measurement. The FT-IR measurement demonstrated that the original structure was destroyed and a new functional group was produced. The Raman spectroscopy revealed that an amorphous carbon phase was induced by ion beam. The XPS results indicate that the atomic percentage of carbon increases with ion fluences for each ion species. The average surface roughness (Ra) increased with the ion fluence when compared with the non-irradiated chitosan film surface. With a fluence of 10¹⁵ ions/cm² all substrates displayed wettability of 70 to 72°.

Key words: Chitosan, Ion beam, Surface modification

1. INTRODUCTION

Chitosan is a partially deacetylated form of chitin, the most abundant natural polymer after cellulose. Nowadays, chitosan has found emerging applications in tissue engineering due to its biocompatibility, biodegradability and low toxicity.

Practical applications of polymers strongly depend on their surface properties. Therefore, many surface modification techniques, including plasma treatment, ultraviolet irradiation, electron beam bombardment and ion implantation, are being used in order to alter the surface properties of materials. Ion implantation has been shown to be a useful technique for improving the surface properties of polymer. It has been used recently for the surface modification of polymers to improve biocompatibility [1-5].

Our previous study indicated that the cell attachment property of chitosan films can be controlled by ion-beam irradiation. In this study, we investigated the surface properties of chitosan film modified by an ion beam. He⁺, N₂⁺, O₂⁺, Ar⁺ and Kr⁺ ion beams were irradiated at an energy of 150 keV with fluences of 10¹³, 10¹⁴, 10¹⁵ ions/cm². The chemical composition, surface topography and wettability at the film surface were characterized by ATR-FTIR, XPS, Raman spectroscopy, AFM and contact angle measurements.

2. EXPERIMENT

2.1 Chitosan film preparation

Chitosan was provided from KIMICA Corporation (DDA : 80 to 90 %, Mw : 124900). Chitosan films were obtained by casting 15 mg/ml chitosan solution (in 2 % acetic acid) at room temperature for 12h. After complete drying, the resulting films were immersed in a dilute ammonia-methanol solution (15 ml 30 % NH₄OH / 35 ml super pure water / 500 ml methanol) for 2 h to neutralize the acid [6]. After the solution was removed, the films were immersed in 70 % ethanol for 12 h.

2.2 Ion-beam irradiation

The chitosan films were irradiated at an energy of 150 keV Kr⁺, Ar⁺, He⁺, O₂⁺ and N₂⁺ ions with fluences of 10¹³, 10¹⁴,

10¹⁵ ions/cm² at room temperature using RIKEN 200 keV ion implanter (RIKEN, Saitama, Japan). The target chamber was maintained at a pressure of 10⁻⁴ Pa during ion-beam irradiation. All irradiated samples were stored in the laboratory atmosphere for at least two weeks before each measurement.

2.3 Surface characterization

2.3.1 AFM

All surfaces roughness measurements were performed using an AFM (Nanoscope, Digital Instruments). The measurement was performed using a tapping mode with a single crystal Si cantilever with a resonant frequency of about 130 kHz. Height images of 10 μm squares samples were taken in an ambient temperature. The arithmetic mean of surface average roughness (Ra) was estimated directly from AFM images. The Ra was calculated from three different areas on each surface and averaged.

2.3.2 FT-IR (ATR)

Chemical analysis was carried out by an Thermo Nicolet Avator 360 FT-IR spectrometer equipped with an Attenuated Total Reflectance (Thermo Nicolet corp., Japan) from 4,000 to 800 cm⁻¹. The spectra were recorded under N₂ at 2 cm⁻¹ resolution and averaged over 32 scans.

2.3.3 Raman spectroscopy

Raman measurements were performed on the samples using a Raman spectrometer (LabRAM, Jobin-Yvon, France) equipped with a He-Ne ion laser (632.817 nm) at a spectral range from 1,000 to 2,000 cm⁻¹.

2.3.4 XPS

The chemical composition of the specimens was measured by an XPS (JEOL, Japan) utilizing a MgKα (1253.6 eV) radiation as an X-ray source at 12 kV and 10 mA. The take-off angle to the substrates was 45°. The operating pressure in the analysis chamber was maintained at below

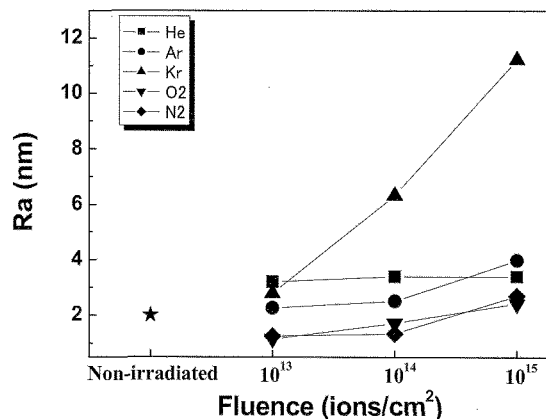


Fig.1. AFM Ra values versus ion beam fluence. Ion species are (a) He⁺, (b) Ar⁺, (c) Kr⁺, (d) N₂⁺ and (e) O₂⁺.

10⁻⁶ Pa during the measurement. Data for the percentage of atomic composition and atomic ratios analysis parameters were calculated using the manufacturer-supplied software.

2.3.5 Contact angle measurement

The surface wettability of each chitosan film was measured using a Contact Angle Meter (Kyowa Interface, Co. Ltd)

equipped with microliter syringe in air at ambient temperature. A distilled water droplet (about 1.0 μl) was dropped onto the surface. The average contact angle value was acquired by measuring at five different positions on the same sample.

3. RESULTS AND DISCUSSION

3.1 Surface roughness

The surface roughness average (Ra) was investigated by an AFM. Figure 1 provides the Ra values from a 10 μm square area as a function of fluence. Except for Kr⁺ implanted film, the Ra values gradually increased with ion fluence. It was found that the modified chitosan film surface forms and roughness changed, depending on the ion species and fluence.

The surface structure and roughness of Kr⁺ irradiated chitosan film was clearly changed (Figure 2). Chitosan film Kr⁺ modified at 10¹⁵ ions/cm² exhibited the roughest surface among all the samples with an average Ra value of 12 nm.

3.2 FT-IR absorption

Figure 3 depicts the FT-IR absorption spectra of He⁺ and Kr⁺ irradiated chitosan films. The FT-IR spectra of Ar⁺, N₂⁺ and O₂⁺ irradiated chitosan films are very similar to those of the Kr⁺ irradiated one. Characteristic bands of chitosan appear at 1,658 cm⁻¹ (C=O stretching), 1,598 cm⁻¹ (-NH₂ bending), 1,382 cm⁻¹ (-CH₂ bending). There are also the absorption

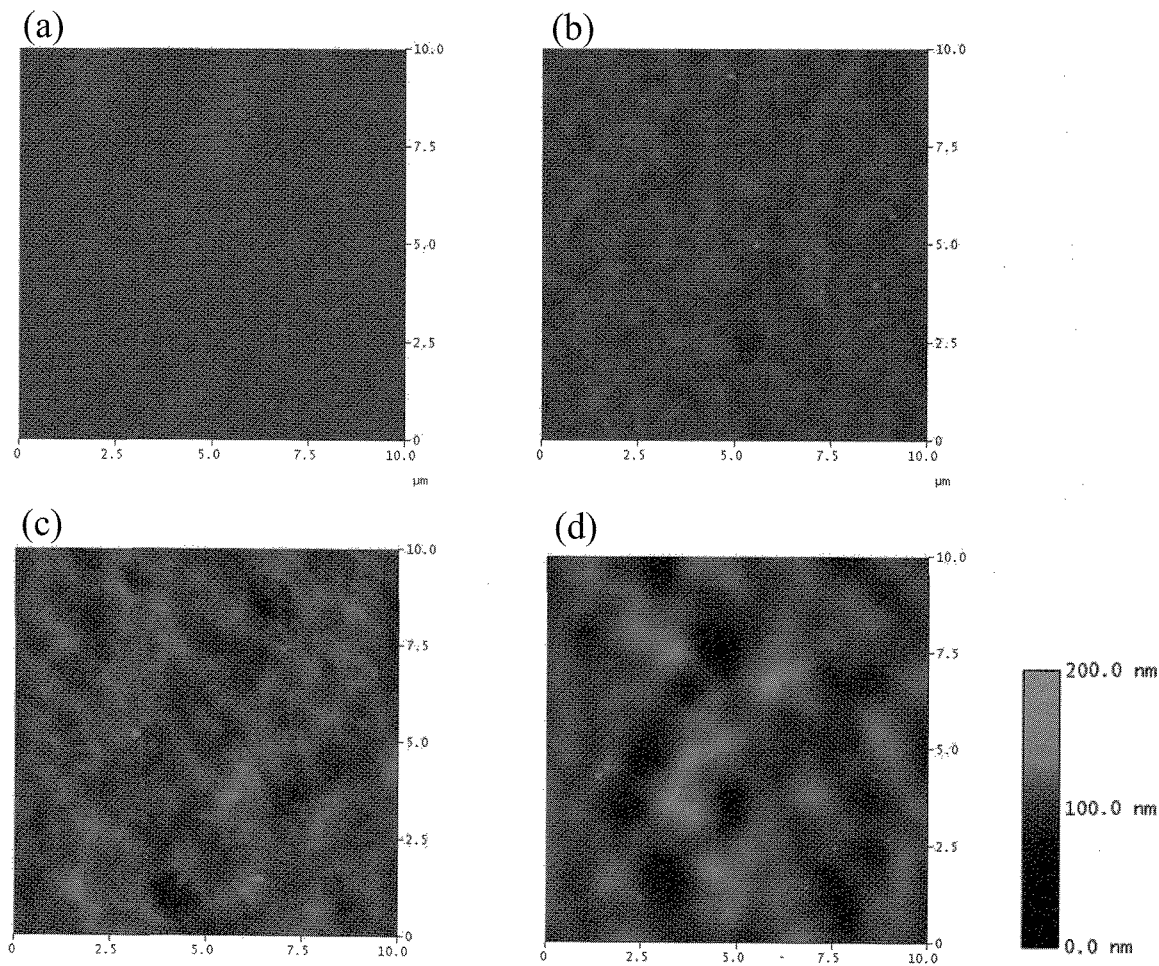
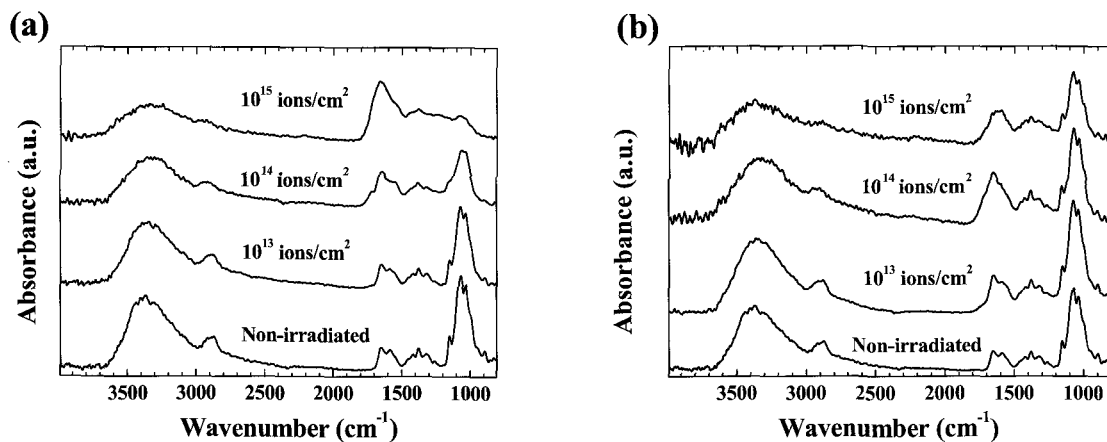


Figure 2. AFM images of (a) non-irradiated chitosan film and films modified by Kr⁺ beam with fluences of (b) 10¹³, (c) 10¹⁴ and (d) 10¹⁵ ions/cm².


 Figure 3. FT-IR spectra of chitosan films modified by (a) He⁺ and (b) Kr⁺ ion

bands at 1,074 and 1,035 cm⁻¹ (skeletal vibrations involving the C-O stretching), 1,157 and 900 cm⁻¹ (anti-symmetric stretching of the C-O-C bridge), which are characteristics of saccharide structure of chitosan [7].

For the spectra (Figure 3) of chitosan film irradiated by He⁺ beam, the peaks at 1,074 and 1,035 cm⁻¹, 1,157 and 900 cm⁻¹ disappeared with ion fluence, suggesting that the He⁺ beam irradiation destroyed the saccharide structure of chitosan. However, for other ion species irradiation, the peaks did not disappear. As the fluence increased to 10¹⁴ ions/cm² for each ion irradiation, the FT-IR spectra indicated that the new band located at 1,722 cm⁻¹ was due to the carboxyl group. The peaks appear for chitosan films irradiated by each ion species at 10¹⁴ ions/cm².

3.3 Raman spectroscopy

Figure 4 presents Raman spectra of non-irradiated film and each ion-implanted chitosan films at a fluence of 10¹⁵ ions/cm². The Raman spectra of chitosan films irradiated with 10¹³ and 10¹⁴ ions/cm² were very similar to the non-irradiated chitosan film. The Raman spectra of the chitosan film irradiated with 10¹⁵ ions/cm² exhibited two new peaks at 1,560 cm⁻¹ and 1,350 cm⁻¹, which can be associated with sp² carbon. The peak at 1,560 cm⁻¹ is characteristic of polycrystalline graphite (G band) or amorphous carbon with graphitic bonding. The peak at 1,350 cm⁻¹ is assigned to disordered graphite (D band). These results demonstrated that each ion irradiation at 10¹⁵ ions/cm² destroyed the natural chitosan film surfaces and produced the amorphous carbon phases.

3.4 Surface chemical composition

The changes in chemical structure of the samples were further investigated by XPS spectra. Table 1 lists the atomic concentrations of carbon, oxygen and nitrogen for all specimens. The C content of chitosan film was increased with

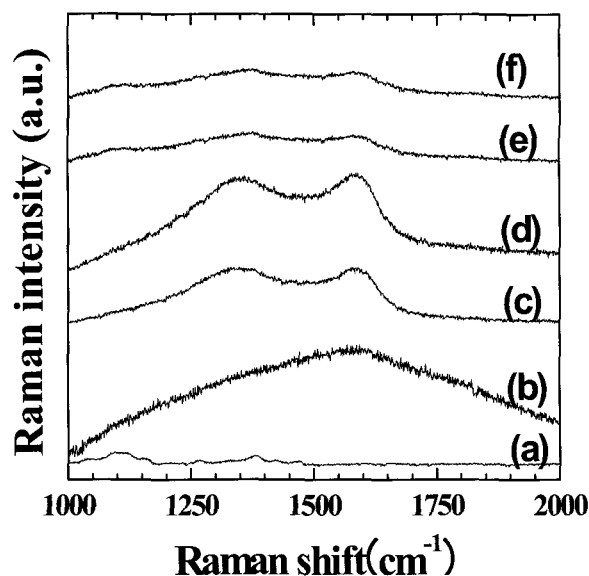

 Figure 4. Raman spectra of (a) non-irradiated chitosan film and (b) He⁺, (c) Ar⁺, (d) Kr⁺, (e) N₂⁺ and (f) O₂⁺ irradiated at 10¹⁵ ions/cm².

Table 1. Changes in elemental composition of chitosan film modified by an ion beam.

Samples	Atomic concentration (%)			
	C	N	O	
original chitosan film	61.17	6.46	32.37	
He ⁺	10 ¹³	61.50	6.12	32.38
	10 ¹⁴	62.91	6.82	30.27
	10 ¹⁵	68.65	6.47	24.88
Ar ⁺	10 ¹³	62.60	5.50	31.90
	10 ¹⁴	66.40	7.10	26.50
	10 ¹⁵	75.89	3.50	20.61
Kr ⁺	10 ¹³	61.73	6.18	32.09
	10 ¹⁴	66.75	7.31	25.94
	10 ¹⁵	77.16	3.63	19.21
N ₂ ⁺	10 ¹³	62.00	5.60	32.31
	10 ¹⁴	63.63	7.60	28.77
	10 ¹⁵	72.25	4.22	23.53
O ₂ ⁺	10 ¹³	62.86	5.95	31.19
	10 ¹⁴	66.03	7.56	26.41
	10 ¹⁵	74.96	3.58	21.46

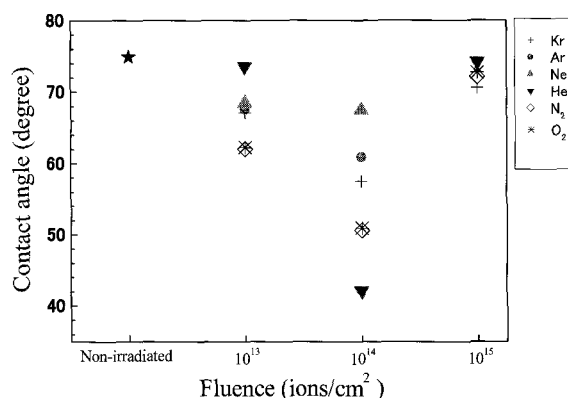


Figure 5. Relationship between ion beam fluence and water contact angle.

ion fluence, while the O atomic percent decreased. It seems that main reason for the increasing C atomic percent is the production of amorphous carbon phases by ion-beam implantations.

3.5 Contact angle measurement

The contact angle of a non-implanted chitosan film surface is about 75°. Figure 5 depicts the water contact angles of samples. It was found that the contact angles decreased with increasing fluences up to 10^{14} ions/cm² for all ion species, which may have been due to the appearance of a hydrophilic group (-COOH) and the decrease of the molecular weight. When the ion beam fluence is 10^{15} ions/cm² for all ion species, the contact angles of samples were 70 to 72°. These values were affected with amorphous carbon phases induced by the ion implantation.

4. CONCLUSIONS

In this study, we investigated the chemical properties of chitosan film surfaces modified by He⁺, Ar⁺, Kr⁺, N₂⁺ and O₂⁺ ions-beam. The results of Raman spectroscopic study indicated that the carbonization was promoted as a fluence increased. XPS measurements revealed that C atomic percentage increased and O atomic percentage decreased with increase of ion fluence. We observed that the C atomic percentages of ion irradiated films increased and induced amorphous carbon phases by ion-beam irradiation. The ion irradiation increased the chitosan film surface roughness with ion fluence increased. In addition, wettability of each film was changed by ion-beam fluences. The contact angles decreased, up to 10^{14} ions/cm². The reasons of the decrease might be production of carbonyl group and decrease of molecular weight by cleavage of functional group such as glycosidic bond. The contact angles of chitosan films irradiated at 10^{15} ions/cm² showed 70 to 72° due to amorphous carbon phases.

In vitro, the microbial adhesion to different substratum surfaces is affected by various physicochemical factors of the substrate, such as hydrophilicity or hydrophobicity and surface roughness. We concluded that surface characteristics can be controlled by ion beam irradiation and cell attachment could be controlled by ion beam irradiation into chitosan film in medical field.

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