Review paper

Effect of ion beam irradiation on the surface properties of biodegradable plastics

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The engineered biodegradable plastics polylactic acid (PLA) and polybutylene succinate (PBS) were irradiated by an ion beam under argon gas and subsequently observed by atomic force microscopy. The PLA and PBS substrates were found to have smooth surfaces after ion beam irradiation with an accelerating voltage of 5 keV. The decomposition rate of the ester group, identified by Fourier transform infrared spectroscopy, increased with increasing acceleration voltage. The quantity of carbide, identified by Raman spectroscopy, was also found to increase with increasing accelerating voltage. It was difficult to observe the D peak. Based on the above results, it was concluded that the carbonization layer (self-carbonization layer) obtained mainly composed of graphite. A Ti thin film was added to the test specimen surface by ion beam mixing, forming a self-carbonization layer, and its adhesion was analyzed by performing a scratch test. High adhesion was obtained at an accelerating voltage of 5 keV. Similar results were obtained for PBS, which has low heat resistance.

Key words: biodegradable plastic, ion beam mixing method, ion beam irradiation, thin film, carbonization layer

1. INTRODUCTION

Alternative commodity plastics possess good characteristics such as low cost, light weight, high durability, and chemical stability. Consequently, they are typically mass-produced and disposed of after use. While chemical stability is an advantageous material property, it adversely affects the global environment because plastics are resistant to decomposition in the environment after they have been used. To overcome this problem, biodegradable resin, which has a low environmental load since it completely degrades into water and carbon dioxide, has been investigated as an alternative material. However, its current usage is limited since it has a high production cost and low heat resistance.

The multiple functions imparted by the addition of a thin film to biodegradable plastics are thought to include improvement of their electrical properties. Hence, this is a promising method to contribute to greater use of biodegradable plastics. In addition, mass production is expected to reduce costs. One method of thin film application, ion beam mixing (IBM), gives a high-adhesion thin film through the formation of a mixing layer. When a biodegradable plastic is used as a substrate, ion beam irradiation produces thermal damage through a combination of low heat resistance and thermal shrinkage due to weak adhesion between the base material and the metal thin film. When ion beam irradiation was carried out using helium ions, a carbonization layer (sometimes referred to as a self-carbonization layer) was found to form under certain irradiation conditions on biodegradable resin surfaces.^[1] The formation of a self-carbonization layer is expected to improve adhesion between biodegradable

plastics and thin films. It is possible that while a thick carbonization layer is formed by small-radius He⁺ ions, the carbonization layer formed by large-radius Ar⁺ ions is thin and of high density. In this study, ion radius affects adhesion, large-radius Ar⁺ ions were used to form a high-density self-carbonization layer, and the fine structure of the resulting layer was evaluated. A Ti thin film was then applied to the biodegradable plastic and the film was examined.

2. TESTING MATERIALS AND EXPERIMENTAL METHODS

2.1 Substrate materials

Poly(lactic acid) (PLA) (Terramac TE-2000, Unitika Ltd.) and poly(butylene succinate) (PBS) (Bionolle #1020, Showa Highpolymer Co., Ltd.) were chosen as biodegradable plastic substrates. They were produced by chemical synthesis.

PLA, which is a hard resin produced from renewable plant-derived materials, has a glass transition temperature (T_g) of 60°C and a melting point (T_m) of 170°C, and is highly transparent. Figure 1 shows the chemical structure of PLA. PBS, a soft resin that takes

Fig.1 Chemical structure of PLA.

Fig.2 Chemical structure of PBS.

the form of a thin, milky-white, translucent plastic, has a T_g of -32°C and a T_m of 114°C . It is a biodegradable plastic with excellent decomposition characteristics. Figure 2 shows the chemical structure of PBS. These two biodegradable plastics were selected as the substrate materials in this study as they have different heat sensitivities and hardness.

2.2 Film formation method and equipment

The method of forming a self-carbonization layer consisted of irradiation of a biodegradable plastic substrate with an ion beam, which induced O and H atoms to migrate out of the substrate, causing the substrate surface to become carbonized. Table I lists the formation conditions for the self-carbonization layer.

Table I Conditions for formation of self-carbonization layer.

Ion species	Ar^+		
Base pressure [Pa]	6.0×10^{-4}		
Current density [$\mu\text{A}/\text{cm}^2$]	20		
Accelerating voltage [keV]	1	5	9
Irradiation time [s]	200		
Water-cooling	Used		

Next, a Ti thin film was applied to the self-carbonization layer by IBM. IBM rearranges the surface atom layers of the substrate and/or mixes ionized atoms or molecules with high energy. Due to the resulting mixing layer, thin films formed by IBM do not have a distinct interface with the substrate. Thus, strong adhesion of the thin film can be realized. Furthermore, this method employs a lower temperature than other thin-film formation methods and, consequently, is suitable for applying films to biodegradable plastics

Table II Conditions for formation of Ti thin film.^[2]

Ion species	Ar^+
Metal species	Titanium
Base pressure [Pa]	5.0×10^{-4}
Argon pressure [Pa]	2×10^{-2}
Accelerative voltage[keV]	1
Current density [$\mu\text{A}/\text{cm}^2$]	20
Deposition rate [nm/s]	0.15
Film thickness [nm]	About 100
Water-cooling	Used

with low heat resistance. Table II lists the conditions for formation of Ti thin films by IBM. Figure 3 shows the IBM configuration used for the formation of the self-carbonization layer and the application of the thin film.

Fig.3 IBM configuration.

The dimensions of the substrate were $10 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$. Ion beam irradiation was carried out on the substrate. After formation of the self-carbonization layer on the substrate surface, the thin film was applied as shown in Figure 4.

Fig.4 Thin film formation process.

2.3 Evaluation of substrate and thin film

The surface morphologies produced by ion beam irradiation with different accelerating voltages were observed by atomic force microscopy (AFM). The structural change induced in the substrate by ion beam irradiation was then analyzed by Fourier transform infrared spectroscopy (FT-IR) and the structure of the self-carbonization layer was analyzed by Raman spectroscopy (RSA). A Ti thin film was then formed on the self-carbonization layer by IBM and the adhesive strength was evaluated by scratch testing.

3. RESULTS AND DISCUSSION

3.1 Effect of ion beam irradiation on surface morphology of biodegradable plastics

Figure 5 shows AFM images of the surfaces of PLA substrates. Table III shows the scan area size and height scale. The AFM results revealed that the surfaces of PLA substrates irradiated at 1 and 5 keV were smooth, due to atomic migration. Thermal damage due to excess energy was observed for the surface irradiated at 9 keV. These results indicate that an accelerating voltage in the range 1–5 keV is optimal for smoothing PLA surfaces. Figure 6 shows AFM images of the surfaces of PBS substrates. Table III shows the scan area size and height scale. The AFM results revealed that no change was induced on the PBS surface by irradiation at 1 keV. The PBS substrate irradiated at 5 keV exhibited smoothing of

Fig.5 AFM images of PLA surfaces.

Fig.6 AFM images of PBS surfaces.

Table III Scan area size and height scale for AFM.

	PLA		PBS	
	Scan area	Height (nm)	Scan area	Height (nm)
(a)	5 μm	116	5 μm	150
(b)	$\times$	700	$\times$	220
(c)	5 μm	300	5 μm	300
(d)	5 μm	15	5 μm	120

* (a) Non irradiation, (b) 1 keV, (c) 5 keV, (d) 9 keV.

the surface due to atomic migration. A round hole was observed on the surface in the AFM image. This suggests hole that atom and/or molecule discharged drastically in substrate surface due to the thermal energy of ion beam irradiation. Thermal damage due to excess energy was observed on the surface irradiated at 9 keV. The results obtained for PLA and PBS indicate that 5 keV is the optimal accelerating voltage for producing smooth surfaces.

3.2 Effect of ion beam irradiation on fine structure of biodegradable plastic

The effect of ion beam irradiation on the fine structure of the biodegradable plastics was investigated by FT-IR. Figure 7 shows structural analyses of the PLA and PBS substrates based on FT-IR spectra (depth resolution 0.1–1 μm).

In Figure 8, it can be seen that P_1 (PLA: 1748 cm^{-1} , PBS: 1714 cm^{-1} , C=O stretching) and P_2 (PLA: 1770 cm^{-1} , PBS: 1733 cm^{-1} , carboxyl stretching) were selectively excited as a result of degradation due to ion beam irradiation. The P_1 to P_2 intensity ratio was

calculated for both PLA and PBS. The density of carboxyl bonds increased with increasing accelerating voltage for ion beam irradiation. The FT-IR results indicate that ion beam irradiation cleaved the ester bond of the biodegradable plastics, increasing the density of carboxyl bonds.

Fig.7 Structural analysis of PLA and PBS by FT-IR: (a) Non irradiation, (b) 1 keV, (c) 5 keV, (d) 9 keV.

Fig.8 Variation of ratio of carboxyl stretching to C=O stretching with accelerating voltage: (a) Non-irradiation, (b) 1 keV, (c) 5 keV, (d) 9 keV.

The methyl (CH_3) group in PLA and the alkane chain in PBS have relatively weak bonds compared to the C–O bond and are of greater length. Calculation of the bond intensity ratios showed that the bond ratio decreased with increasing accelerating voltage for both PLA and PBS. Therefore, the production of carbide increased; as this occurs upon decomposition of biodegradable plastics, it was concluded that a carbonization layer had been formed.

3.3 Confirmation of fine structure of carbonization layer formed by ion beam irradiation

The fine structure of the self-carbonization layer was investigated by RSA (depth resolution 1–5 μm).

Figure 9 shows structural analysis of the self-carbonization layers by RSA. The D peak is not visible. Figure 10 shows that P₃ (PLA: 1773 cm⁻¹, PBS: 1727 cm⁻¹, C=O stretching) and P₄ (PLA: 1584 cm⁻¹, PBS: 1585 cm⁻¹, G peak) were selectively excited with increasing intensity of the G peak.

Fig.9 Structural analysis of self-carbonization layer by RSA: (a) Non irradiation, (b) 1 keV, (c) 5 keV, (d) 9 keV.

Fig.10 Variation in G peak intensity with accelerating voltage: (a) Non irradiation, (b) 1 keV (c) 5 keV, (d) 9 keV.

The P₃ to P₄ intensity ratio was calculated for both PLA and PBS. The intensity of the G peak increased with increasing accelerating voltage of the ion beam irradiation. The G peak appeared at voltages of more than 5 keV. The RSA results indicated the formation of a self-carbonization layer by ion beam irradiation, while the appearance of the G peak showed that the surface comprised graphite.

3.4 Effect of self-carbonization layer on adhesion of Ti thin film

In the scratch test investigation, the curvature radius of the indenter was 100 μ m, the material was diamond,

the scratch speed was 0.65 mm/sec, and Load_{max} was 150 gf. Furthermore, the scratch test was compliant with JIS 3255. The tests revealed that the self-carbonization layer had an effect on the adhesion of the Ti thin film. Figure 11 shows the adhesion of the Ti thin film as determined by the scratch test. The highest critical load (L_c) value for PLA was obtained by irradiation at 5 keV,

Fig.11 Critical load (Lc) variation determined by scratch test of Ti thin film.

followed by 9 keV irradiation, no irradiation, and 1 keV irradiation. Thus, the highest adhesion for PLA was obtained by 5 keV ion beam irradiation. 5 keV irradiation is strong chemical adhesion for addition thin film than 1 keV irradiation, adhesion is possible advancement. As the adhesion obtained by 1 keV irradiation was lower than that obtained at 5 keV, surface after 1 keV irradiation was not fit for modification. Similar results were obtained for PBS, which has low heat resistance. The scratch test results revealed that, for both PLA and PBS, the optimal ion beam irradiation accelerating voltage for the formation of a carbonization layer with high adhesion was 5 keV.

Adhesion thinks enhancing by three factors of next. ① Both polymer and metal thin film has flexible carbonization layer than metal, ② it has chemical bond of TiC et cetera, ③ a mixing layer of C and Ti with a concentration gradient is formed.

4. CONCLUSIONS

The results of this study clearly demonstrated that Ti film adhesion can be enhanced by the presence of a self-carbonization layer. Furthermore, even for materials with different heat susceptibilities, the carbonization layer had a similar effect on the adhesion of the Ti thin film.

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