SURFACE MODIFICATION OF DENTAL DEVICES

Surface Analysis of Plasma-based Fluorine and Silver Ion Implanted & Deposited Acrylic Resin

Yukari Shinonaga, Kenji Arita and Milanita E. Lucas
Department of Pediatric Dentistry, Institute of Health Biosciences, The University of Tokushima Graduate School Tokushima, Japan

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Abstract: The aim of this study was to modify acrylic resin (PMMA) with fluorine (F) and silver (Ag) dual ions by a hybrid process of plasma-based ion implantation & deposition (PBII-D), and to enable the surface of the devices inhibition of bacterial adhesion. The surface characteristics, hydrophobic property and brushing abrasion resistance were evaluated by XPS analysis, contact angle measurement and brushing abrasion test. F and Ag were implanted-deposited and have formed carbon-fluoride and Ag-deposited layer on the surface of the PMMA plate. The contact angle of F+Ag implanted-deposited PMMA was increased compared with non-treated control and F only deposited PMMA. After 60,000 brushing strokes, the contact angle of modified PMMA remained to be higher than that of the control PMMA. This study indicated that F+Ag implantation-deposition has improved the hydrophobic property of acrylic resin and was sustained even after routine tooth brushing.

1 INTRODUCTION

Bacterial colonization and subsequent device infection are common complications of medical and dental devices (Gristina, 1987). Especially, acrylic base plates for prosthodontics, orthodontics and pedodontics are exposed to oral microbial flora to include bacteria, viruses, and fungi, and are susceptible to adhesion of bacterial plaque. Oral bacteria can be released from denture plaque into salivary secretions and then aspirated into the lower respiratory tract causing pneumonia (Sumi, 2007). Among patients, the most general method for the removal of denture plaque is brushing. However, effective plaque removal requires a degree of manual dexterity that is often lacking especially among elderly and individuals with disabilities. Therefore, it is important to modify the acrylic resin denture surface to enable inhibition of oral bacterial adhesion.

Plasma-based ion implantation (PBII) is a promising method for the surface modification of three-dimensional materials (Conrad, 1987). In particular, the ion deposition with simultaneous ion implantation (plasma-based ion implantation and deposition: PBII-D) is desirable for efficient processing and has an advantage over conventional methods (Kuze, 2002).

Recently, several researchers have carried out the surface modification using fluorine (F) ion and found it to be a useful means of inhibiting bacterial adhesion (Zhao, 2007 and Nurhaerani, 2007). In addition, it is well known that silver (Ag) possesses the antibacterial property without any toxic effects in comparison to other heavy metal ions. We developed the new technology to simultaneously implant and deposit both F and Ag ions into dental and medical devices using PBII-D. The aim of this study was to examine the effectiveness of both F and Ag ions implanted-deposited into acrylic resin by evaluating the surface characteristics and brushing abrasion resistance.

2 MATERIALS AND METHODS

2.1 Preparation of Specimens

Poly methyl methacrylate (PMMA) (Clarex 000, Nitto Jushi Kogyo, Co., Ltd., Tokyo, Japan) plates

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with measurements of 10mm×10mm×1mm were used. The PMMA plates were modified by plasma-based ion implantation-deposition equipment at Plasma Ion Assist Co., Ltd., Kyoto, Japan. Fluoride gas used for F ion implantation-deposition was perfluoropropane (C_3F_8). For Ag ion implantation-deposition, a 99.8 % Ag mesh cover was set 10mm above the plates and sputtered by C_3F_8 gas. The conditions of plasma-based F and Ag dual ion implantation-deposition are shown in Table 1.

Table 1: The condition of fluorine and silver ion implantation-deposition into PMMA plates.

Group	Conditions	Implantation process	Deposition process
Control	Voltage (keV) Time (min) Ag mesh	0 0 unused	0 0 unused
F deposited	Voltage (keV) Time (min) Ag mesh	0 0 unused	-0.5 60 unused
F+Ag implanted-deposited	Voltage (keV) Time (min) Ag mesh	-5 30 used	-0.5 60 used

2.2 Surface Shemical Analysis by XPS

The surfaces of the control, F deposited and F+Ag implanted-deposited PMMA were characterized by X-ray photoelectron spectroscopy (XPS). XPS spectra were obtained using an X-ray photoelectron spectrometer (ESCA-850, Shimadzu Co., Kyoto, Japan) with Al-Kα radiation operated at 30 mA current and 7 kV accelerating voltage. Specifically, depth profile analysis for the F+Ag implanted-deposited PMMA was performed using Ar etching under the pressure of 5×10^{-4} Pa. The Ar etching rate was approximately 6 nm/min on Ag.

2.3 Contact Angle Measurements

Specimens were ultrasonically cleaned in distilled water for 10 minutes, and then dried at room temperature before contact angle measurement. Static contact angle measurements were conducted by the sessile drop technique using a contact angle meter (CA-DT, Kyowa Kaimenkagaku Co. Ltd., Saitama, Japan) with three test liquids: distilled water, diiodomethane and ethylene glycol at room temperature. One point per specimen was measured (N=5/group, *i.e.* 5 points/group). The surface free energies of specimens were calculated from the contact angles with the three test liquids (Liu, 2005).

2.4 Brushing Abrasion Test

The brushing abrasion test machine (MANA-63S, MASUDA Co., Osaka, Japan) was used. A commercial toothbrush (Dr. Bee Young ⅡS, Bee Brand Medico Dental Co., Ltd., Osaka, Japan) was attached to the toothbrush holder in contact with the F deposited and F+Ag implanted-deposited PMMA set on the sample holder. Distilled water without dentifrice was then poured into the vessel, and the machine was run at 80 rpm with a 200 g load. The water contact angle measurements of the F deposited and F+Ag implanted-deposited PMMA were done every 10,000 strokes up to 60,000 strokes. In the control PMMA, the contact angle was measured without brushing. Five points per specimen were measured.

2.5 Statistical Analysis

The results of the contact angle measurements before and after the brushing abrasion test were expressed as the mean ± standard deviation. The data were analyzed using one-way ANOVA and Scheffe's multiple comparison tests (α = 0.05).

3 RESULT

3.1 XPS Analysis

XPS wide-scan spectra of the control, F deposited and F+Ag implanted-deposited PMMA are shown in Figure 1. The peaks of C1s and O1s were detected in the wide-scan spectrum of the control PMMA. Moreover, F1s peak appeared on the F deposited PMMA surface; and F1s, Ag3d and Ag3p peaks appeared on the F+Ag implanted-deposited PMMA surface. The F1s and Ag3d XPS depth profiles of the

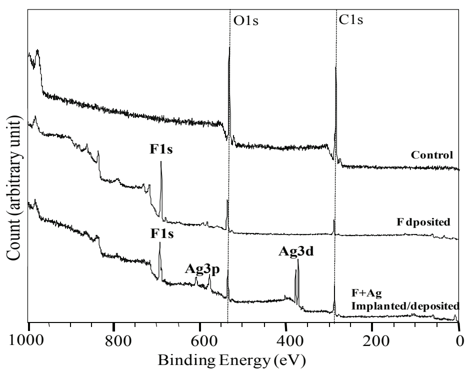

Figure 1: XPS wide-scan spectra of PMMA specimens.

F+Ag implanted-deposited PMMA are shown in Figure 2. The chemically shifted peaks of F1s from surface to 7 minutes Ar etching depth are observed in the higher binding energy region (689-690 eV). The higher values was close to the reported binding energy of p-(CF_2=CF_2) (689 eV) (Briggs and Seah, 1990).The F1s peak decreased as the Ar etching increased and was not detected after 15 minutes of Ar etching. Ag3d peak was also detected after Ar etching for about 15 minutes in Ag3d depth profile. In F1s and Ag 3d depth profiles, the peaks of AgF were not detected.

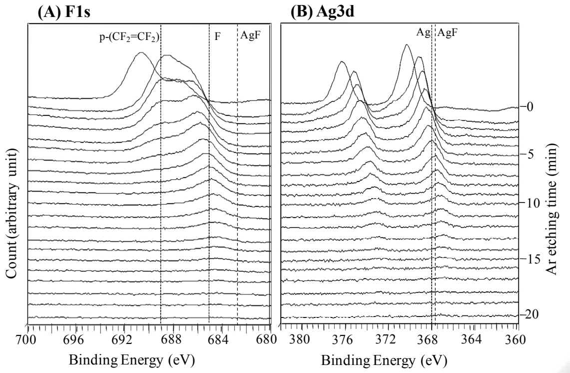

Figure 2: F1s (A) and Ag3d (B) XPS depth profiles of the F+Ag implanted-deposited PMMA. Dashed lines show the binding energy value of p-(CF_2=CF_2): 689.0 eV, F: 685 eV and AgF: 682.7 eV in the F1s depth profile (A), and Ag: 368.2 eV and AgF: 367.7 eV in the Ag3d depth profile (B). The values were based from Briggs and Seah, (1990).

3.2 Surface Energy Analysis

The contact angles of three test liquids: distilled water (W), diiodomethane (Di) and ethylene glycol (EG) and the calculated surface free energy values of control, F deposited and F+Ag implanted-deposited PMMA are shown in Table 2. The contact angles of all test liquids on the F deposited and F+Ag implanted-deposited PMMA were significantly higher than that of the control PMMA (p<0.01). Moreover, the contact angle of all test liquids on the F+Ag implanted-deposited PMMA was higher than that of the F deposited PMMA (p<0.001). The surface free energy of the F+Ag implanted-deposited PMMA was lower than that of the control and F deposited PMMA.

Table 2: Contact angle and surface free energy of PMMA specimens.

Group	Contact angle θ (degree)			Surface free energy (mJ/m^2)
	θ^W	θ^{Di}	θ^{EG}	
Control	64.4°	36.3°	50.8°	44.05
F deposited	100.0°	52.2°	62.7°	33.77
F+Ag implanted/ deposited	123.9°	82.3°	95.2°	20.65

3.3 Brushing Abrasion Test

In the F deposited and F+Ag deposited PMMA, the contact angles after 10000, 30000 and 60000 brushing strokes were significantly lower than before brushing (p<0.001). The contact angle of the F+Ag implanted-deposited PMMA was not significantly different compared with that of the F deposited PMMA for the same number of brush strokes. However, the contact angles of the F deposited and F+Ag implanted-deposited PMMA after the brushing abrasion test resulted in a significantly higher contact angle compared to that of the control PMMA (p<0.001).

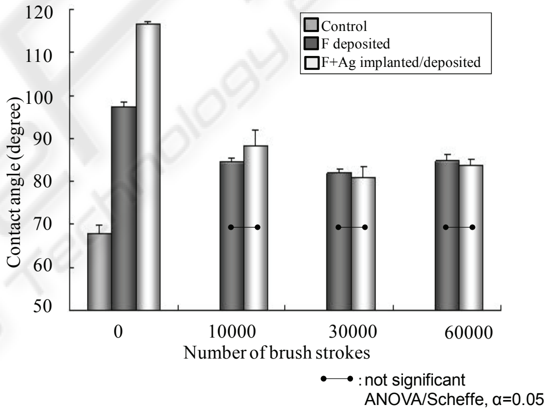

Figure 3: Contact angles of distilled water on the F deposited and F+Ag implanted-deposited PMMA before/after the brushing abrasion test. Horizontal lines indicate no significant differences (ANOVA/ Scheffe, α=0.05).

4 DISCUSSIONS

In this study, we have attempted to modify the surface of PMMA by the simultaneous F and Ag ion implantation-deposition by PBII-D process.

The results have shown that F and Ag were detected on the surface of the F+Ag implanted-deposited PMMA by XPS analysis (Figure 1). The existence of carbon-fluoride complexes, such as p-(CF_2=CF_2), and Ag were also detected on the F+Ag implanted-deposited PMMA surface. Moreover, F and Ag were deposited on the surface and implanted to about 90 nm depth (Figure 2). All these suggested that both F and Ag ion implantation-deposition method by PBII-D was applicable to PMMA. In ion implantation-deposition of insulating materials such as PMMA, electric charge-up could be a serious problem, which damages the specimens. In this study, it was thought that Ag mesh was used not only for providing Ag ions but also for decreasing the electric charge-up on the specimens by providing electrons.

It was reported that some properties are specific to the inert surface, such as the surface free energy, surface charge, hydrophobic property, surface roughness and surface chemistry (Perini, 2006). One approach in the attempt to reduce the bacterial colonization is to modify the surface free energy and chemistry. The contact angle is characteristic of the surface energy of a solid surface, and has been used for determining the wettability and hydrophobic property of various solid materials. Bacterial adhesion is energetically unfavourable, if the solid surface free energy is less than 50 mJ/m^2 (Busscher, 1984). In this study, the surface free energy of the F+Ag implanted-deposited PMMA was 20.65 mJ/m^2 (< 50mJ/m^2), which may imply potential inhibition of bacterial adhesion by hydrophobic mechanism. In addition, the negative relationship between the contact angle and the bacterial adhesion property was reported (Zhao, 2007, and Nurhaerani, 2007). In the present study, the contact angle of the F+Ag implanted-deposited PMMA after 60,000 brushing strokes was significantly higher than that of the control PMMA. Kanter *et al.* (1982) estimated that 20,000 brushing strokes were the equivalent to approximately 5 years of brushing. The present study confirmed that the high contact angle of the F+Ag implanted- deposited PMMA could remain after the equivalent of 15 years of brushing with a toothbrush. These results suggested that dual F and Ag implantation-deposition could possibly inhibit the bacterial adhesion to the PMMA devices by increasing the contact angle and decreasing the surface free energy.

These results suggested that both F and Ag ion implantation-deposition by PBII-D process was the superior surface modification method for acrylic materials to inhibit bacterial adhesion.

5 CONCLUSIONS

In this study, PMMA plates were simultaneously implanted-deposited with both F and Ag ions by a hybrid process of PBII-D. The F+Ag implanted-deposited PMMA surface has obtained low surface free energy (20.65 mJ/m^2) and the presence of carbon-fluoride complexes and Ag on the surface was indicated. Moreover, due to the presence of both F and Ag ions, the hydrophobic properties remained after brushing with a toothbrush. These results suggested that both F and Ag ion implantation-deposition by PBII-D has the potential to give the medical and dental devices antibacterial qualities.

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