

Improved brushing durability of titanium dioxide coating on polymethyl methacrylate substrate by prior treatment with acryloxypropyl trimethoxysilane-based agent for denture application

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The purpose of this study was to determine whether the brushing durability of a titanium dioxide coating on a polymethyl methacrylate (PMMA) substrate was improved by prior treatment with an acryloxypropyl trimethoxysilane-based agent. Titanium dioxide coatings were obtained by spray-coating substrates with or without prior treatment. Structure was investigated using IR, SEM, and an EPMA. Effect on durability against brushing was determined with a brush-wear test machine utilizing a commercial denture brush.

A thin layer comprised of siloxane and TiO₂ was formed on a PMMA substrate by prior treatment with an acryloxypropyl trimethoxysilane-based agent and spray-coating of TiO₂. Prior treatment demonstrated improved stability against brushing, whereas the titanium coating was removed after less than 1×10⁵ brushing cycles without prior treatment. This suggests that prior treatment with an acryloxypropyl trimethoxysilane-based agent would confer improved durability against brushing-induced stress on a TiO₂ coating in its application to dentures.

Keywords: Brushing wear, Surface morphology, Titanium dioxide

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INTRODUCTION

Coating a titanium oxide layer onto a substrate can confer biomedical materials with desirable properties such as high biological affinity and bioactivity¹⁻⁷. Such coatings have also attracted great interest in terms of the potential for practical application offered by their antimicrobial and antifouling properties^{8,9}, as titanium dioxide (TiO₂) induces oxidization on excitation by ultraviolet irradiation¹⁰⁻¹². In dentistry, these properties are particularly useful, as dentures require clean surfaces¹³⁻¹⁷. A TiO₂ layer on a polymethyl methacrylate (PMMA) substrate may allow the development of a new type of denture which is more sanitary and easier to clean¹⁸. Such a TiO₂ layer would need to be capable of bonding strongly to its substrate in order to be highly resistant to friction caused by robust cleaning and brushing.

Many researchers have attempted to fabricate a TiO₂ coating on a polymer or metal substrate by using sol-gel techniques^{5-7,18-21}. Bonding strength with metals, ceramics and polymers was generally improved by treatment with silane-coupling agents such as 3-glycidoxypropyl trimethoxysilane, 3-isocyanatopropyl triethoxysilane, and 3-methoxypropyl trimethoxysilane prior to application of TiO₂^{5-7,20,21}. The adhesion of a TiO₂ coating to a substrate needs to be reliable long-term if it is to be applied to dentures. Durability against friction caused by brushing is of particular importance^{8,9,18,22}. However, to the author's knowledge, no studies have investigated the durability of a TiO₂ coating on a PMMA substrate under a friction-simulating brushing process.

The present study focuses on the durability of a TiO₂ coating on a PMMA substrate in response to brushing stress in a denture model utilizing a brush-wear test machine equipped with a commercially available denture brush. First, the structure and chemical characteristics of the coating, with or without prior treatment, and its interface with the PMMA substrate were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and element analysis using an electron probe microanalyzer (EPMA). Next, durability of the TiO₂ coating on the PMMA substrate was investigated in a practical model. The TiO₂ coating was subjected to simulated stress in a brush-wear test machine utilizing a commercially available denture brush, followed by SEM-EPMA to evaluate its resistance to friction.

MATERIALS AND METHODS

(1) *Characterization of TiO₂ coating on PMMA substrate*
PMMA substrates were prepared from a commercial acrylic resin for dentures (Acron, GC Corporation, Tokyo) by a heat-curing procedure. PMMA powder was mixed with methyl methacrylate (MMA) monomer at a volume ratio of 2:1 = PMMA:MMA, and the resulting paste filled into an epoxy mold (22 mm in diameter and 23 mm in height: EX-ring, Refine Tech, Kanagawa, Japan). The paste was put at 60°C for 30 min due to primary polymerization, and then put in boiling water for 30 min due to secondary polymerization. To obtain an ideal interface between the TiO₂ coating and PMMA substrate, the surface of the substrate was polished

with #1200 silicon carbide abrasive paper and polished with a 0.3- μm alumina suspension. The polished specimens were then ultrasonically washed in distilled water for 10 min.

A TiO_2 coating was applied to both sets of specimens, with or without prior treatment with a type of silane-coupling agent, hereafter, referred to as siloxane primer (SP). In SP treatment, a commercial agent (PO-3000, Nihon Parkerizing, Kanagawa, Japan), which mainly composed of acryloxypropyl trimethoxysilane (4.5% converted for SiO_2) in ethanol, was sprayed on to the PMMA substrate for 2 s with an air brush gun (Super airbrush advance, WAVE, Tokyo, Japan), after which, it was dried in an oven for 10 min at 70°C in air atmosphere. The commercial agent (Paltitan PTI5603, Nihon Parkerizing, Kanagawa, Japan), which contains 2.0% anatase-type TiO_2 in water and ethanol, was used for the TiO_2 coating (TC). The coating was sprayed on to the substrate for 2 s, after which, it was dried in an oven for 10 min at 70°C. The 3 types of specimen prepared were referred to as SP-treated (siloxane primer only), TC-treated (TiO_2 -coating only), and SP+TC-treated (both siloxane primer and TiO_2 -coating). Surface structure was investigated in all 3 types of specimen. Specimens were characterized by Fourier transformed infrared (FT-IR) spectroscopy. The FT-IR spectrum was determined with the infrared spectrometer (FT/IR 430, JASCO, Tokyo) equipped with a microscope (MICRO-20, JASCO, Tokyo) at 4 cm^{-1} resolution. Crystalline phases in the specimens were analyzed by X-ray diffraction (XRD) using X-ray diffraction device (RINT 2500, Rigaku, Osaka, Japan) operated at 40 kV and 200 mA. Surface morphology and composition were determined by observation under a field emission scanning electron microscope (SEM; ERA-8900FE, Elionix, Tokyo, Japan) and an electron probe X-ray microanalyzer (EPMA; JXA-8200, JEOL, Tokyo, Japan). Cross-sectional views were also observed to determine surface characteristics after the following preparation: the specimens were cut into small pieces and embedded in an epoxy mold with a self-curing epoxy resin (Scandiplex, Scandia, Hagen, Germany). The surface was then mirror-polished with buff and a 0.3- μm alumina suspension. After the specimens were sputter-coated with gold, SEM observations were performed at an accelerating voltage of 15 kV. Mapping analysis of silicon (Si), titanium (Ti), carbon (C) and oxygen (O) was performed with the EPMA at an accelerating voltage of 15 kV.

2) Brush-wear test of TiO_2 coating on PMMA

The durability of the TiO_2 coating on the TC- and SP+TC-treated PMMA substrates in response to brushing stress was evaluated. Our aim was to establish a clinical model which would resemble normal use-conditions as closely as possible. To achieve this, we first prepared PMMA substrates by polishing with #1000 silicon carbide abrasive paper only, followed by ultrasonic washing in distilled water for 10 min. Next, we further prepared two types of PMMA substrate: one

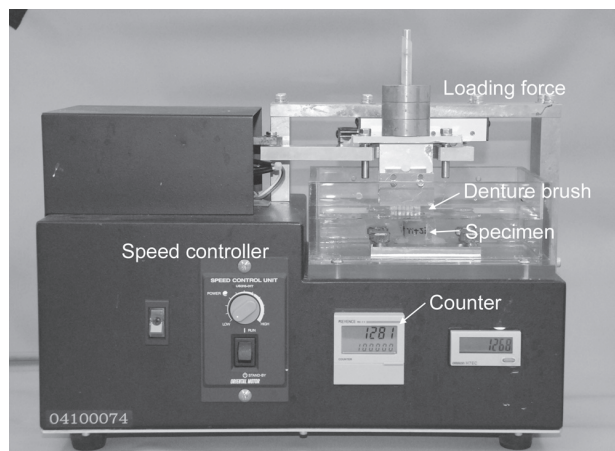


Fig. 1 Brush-wear test apparatus equipped with denture brush and specimen. Loading force was 300 gf, and gliding speed was 150 cycles per 60 s.

with a TC coating only, and the other with both SP treatment and TC coating. Both types of substrate were then subjected to a brush-wear test with a brush-wear test machine (K236, Tokyo Giken, Tokyo, Japan) equipped with a denture brush (Liodent Denture Brush, Lion Dental Products, Tokyo, Japan) to simulate brushing-induced friction, as shown in Figure 1. The brush was positioned so that the bristles were perpendicular to the surface of the specimen, and was applied at a force of 300 gf. The gliding speed of the machine was set to 150 cycles per 60 s. Brushing was continued until distinct frictional evidence was observed. The TC-treated specimens were brushed for 1×10^4 or 1×10^5 cycles, and the SP+TC-treated specimens for 1×10^5 or 2×10^5 cycles. Compositional changes were determined by calculating the atomic ratio of titanium to carbon (Ti/C) in the specimens. The Ti/C ratio was obtained from 10 locations on each specimen. Compositional mapping analysis using the EMPA under SEM observation was also performed on the surface of specimens after the brush-wear tests. Ten specimens were tested in each group. The Ti/C ratio in the TC-treated and SP+TC-treated specimens at before and after brushing was statistically analyzed using a one-way analysis of variance, and a comparison between before and after brushing was made using the Bonferroni test. Statistical significance was set at $\alpha=0.05$ for all data obtained, as determined by statistical analysis software (SPSS 11.0J for Windows, SPSS Inc, Illinois, USA).

RESULTS

1. Surface and morphology of TiO_2 coating on PMMA substrate

Figure 2 shows the FT-IR spectra of each specimen and difference spectra subtracted from the spectra of the non-treated, SP-treated and SP+TC-treated specimens.

All spectra showed peaks at close to 1150, 1240, 1450 and 1720 cm^{-1} originating in the C-C and $-\text{CH}_3$ methacrylate groups of the PMMA²³. The difference spectra showed peaks at close to 1110 cm^{-1} , indicating the presence of Si-O-Si and Si-O-C of silicate or siloxane on SP-treated and SP+TC-treated specimens. The XRD patterns of each specimen showed halo peaks at close to 28° (data not shown), indicating no distinct crystalline structures. This indicates that the coating

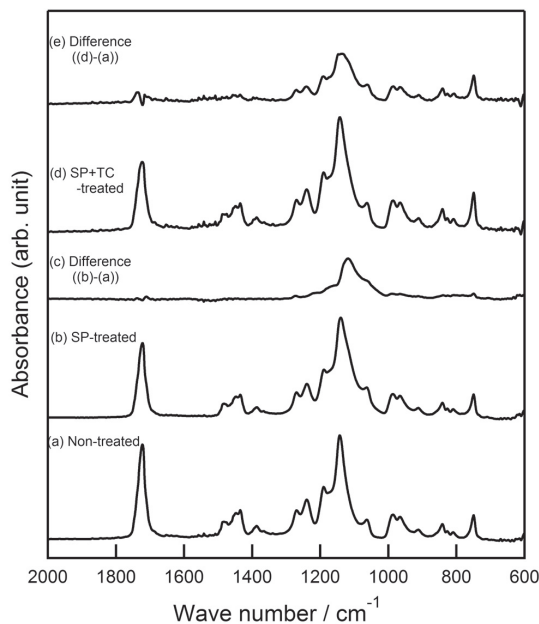


Fig. 2 FT-IR spectra ((a), (b), (d)) and difference spectra ((c) and (e)) subtracted from spectra of non-treated, SP-treated and SP+TC-treated specimens. SP: Siloxane primer. TC: TiO_2 coating

was too sparse in terms of thickness and/or volume to be detected on the specimens.

Figure 3 shows SEM images of the surface and cross-section in each specimen. The SP-treated specimens (Figure 3(b)) showed a rougher surface than the non-treated PMMA substrate specimens (Figure 3(a)). A large number of fine grains were confirmed on the TC-treated specimen, as shown in Figure 3(c). Additionally, part of the specimen showed aggregated particles resembling islands. On the other hand, the SP+TC-treated specimen had a smoother surface than the SP-treated specimens (Figure 3(d)). As shown in Figures 3(f), (g), and (h), layers were clearly visible in the SP-treated, TC-treated and SP+TC-treated specimens, whereas the non-treated specimen showed no such a layer in Figure 3(d). The thicknesses of these layers by SP treatment (Figure 3(f)) and TC treatment (Figure 3(g)) were 2- μm and 1- μm , respectively. The SP+TC-treated specimens had an approximately 2- μm thick layer which then divided into two layers (Figure 3(h)).

Figure 4 shows SEM image and mapping images from the EPMA analysis of the cross-section of an SP+TC-treated specimen. Two layers between acrylic and epoxy resins on SEM image were seen as well as Figure 3(h). Silicon, Ti, and O were predominantly observed throughout all layers. Both the top and bottom layers contained Si and O (Figures 4(b) and 4(d)). Titanium was revealed only in the top layer.

2. Evaluation of TiO_2 coating on PMMA substrate by brush-wear test

Number of brushing cycles was terminated at 1×10^5 and 2×10^5 in TC-treated and SP+TC-treated specimens, respectively, as they showed clear evidence of surface scratching at this point. The TC-treated specimens began to show distinct traces of scratching after only

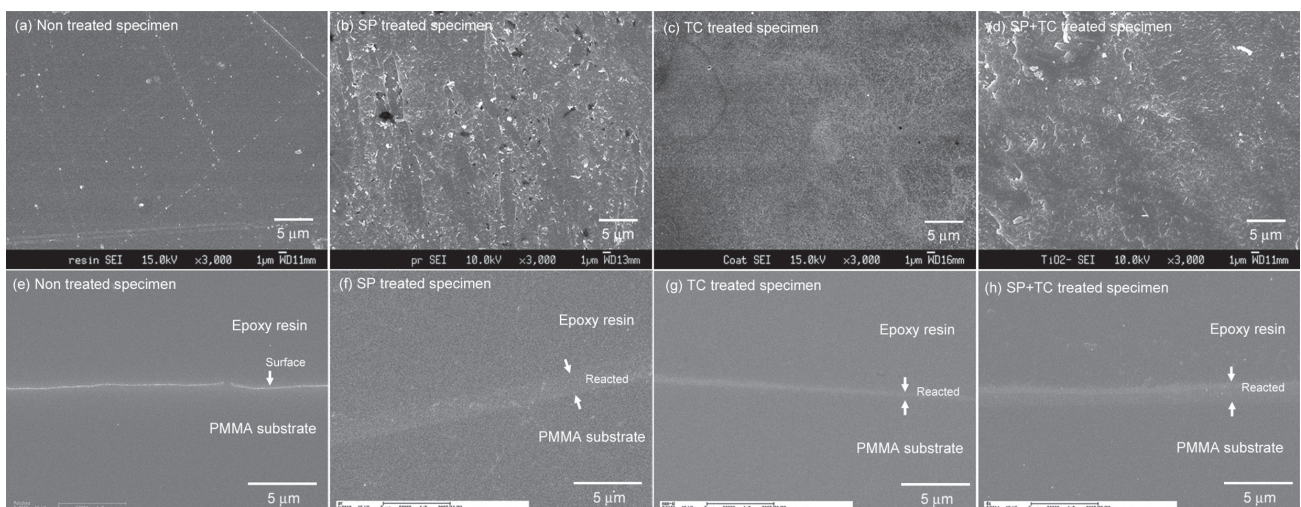


Fig. 3 SEM images of specimen surfaces ((a), (b), (c), and (d)) and cross-sectional structures ((e), (f), (g), and (h)). (a) and (e): non-treated PMMA substrate; (b) and (f): SP-treated PMMA substrate; (c) and (g): TC-treated PMMA substrate; (d) and (h): SP+TC treated PMMA substrate. SP: Siloxane primer. TC: TiO_2 coating

1×10⁵ brushing cycles, whereas the SP+TC-treated specimen showed little sign of scratching at this point. Measurement of Ti/C atomic ratio by EPMA analysis revealed clear degradation of the TiO₂ coating after brushing, especially on the surface of the specimens, revealing traces of scratching, even on visual

observation. Figures 5(a) and 5(b) show a comparison of the Ti/C ratio in the TC-treated and SP+TC-treated specimens in terms of number of brushing cycles, respectively. The values of Ti/C ratios in the TC-treated specimens at before brushing and at after 1×10⁴ and 1×10⁵ brushing were 0.036 ± 0.007, 0.031 ± 0.014

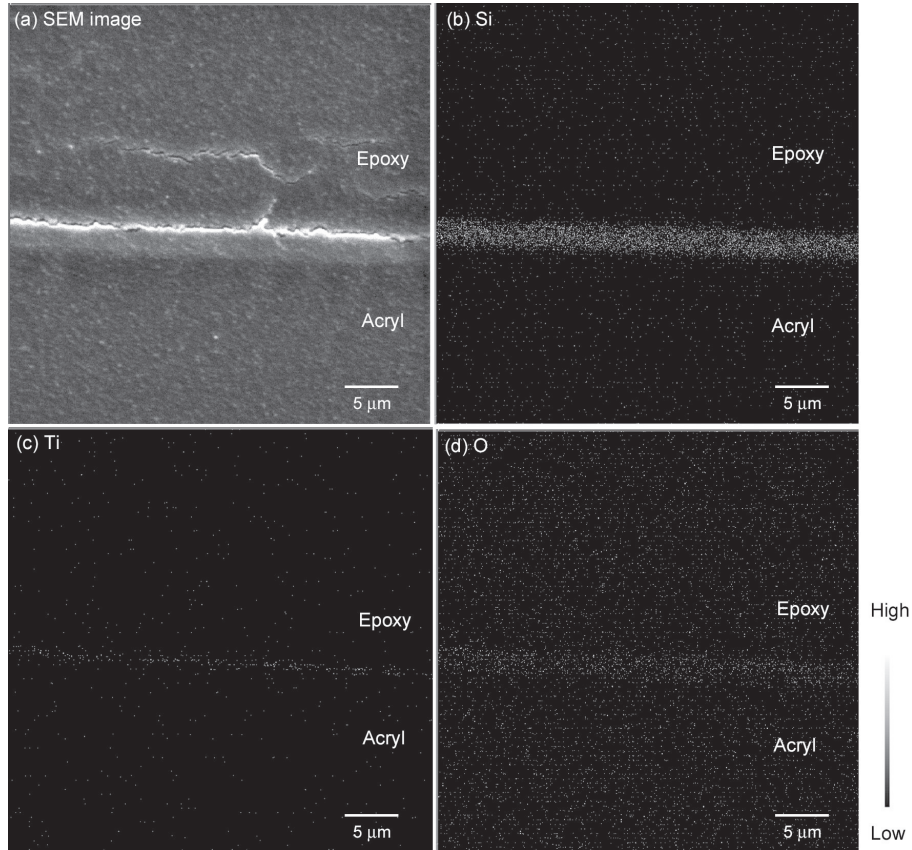


Fig. 4 EPMA mapping analysis of cross-sectional SP+TC-treated specimen. (a) SEM image, (b) Si, (c) Ti, and (d) O

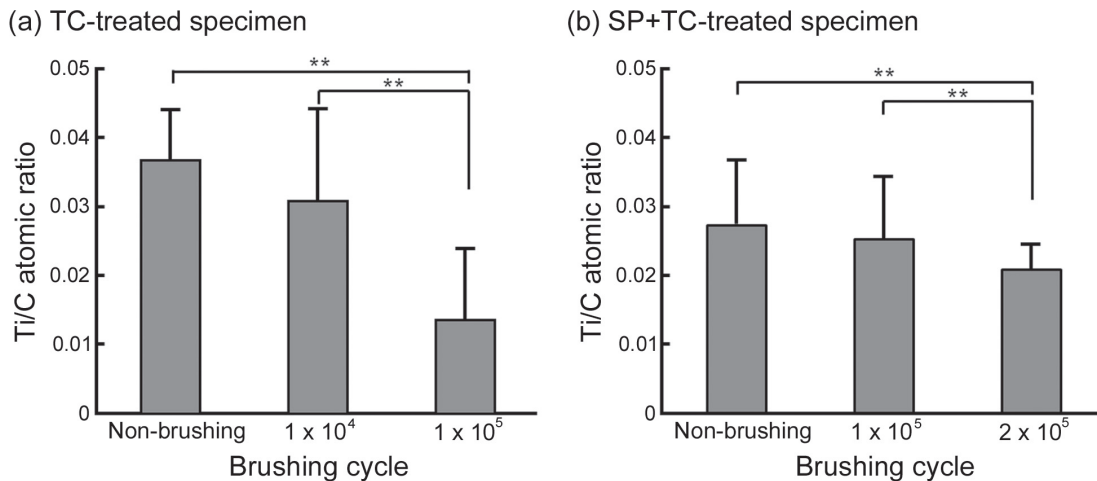


Fig. 5 Comparison of Ti/C atomic ratios between at before and at after brush-wear test. (a) TC specimen (b) SP+TC specimen **: *p* < 0.01 bar: Standard deviation. SP: Siloxane primer. TC: TiO₂ coating.

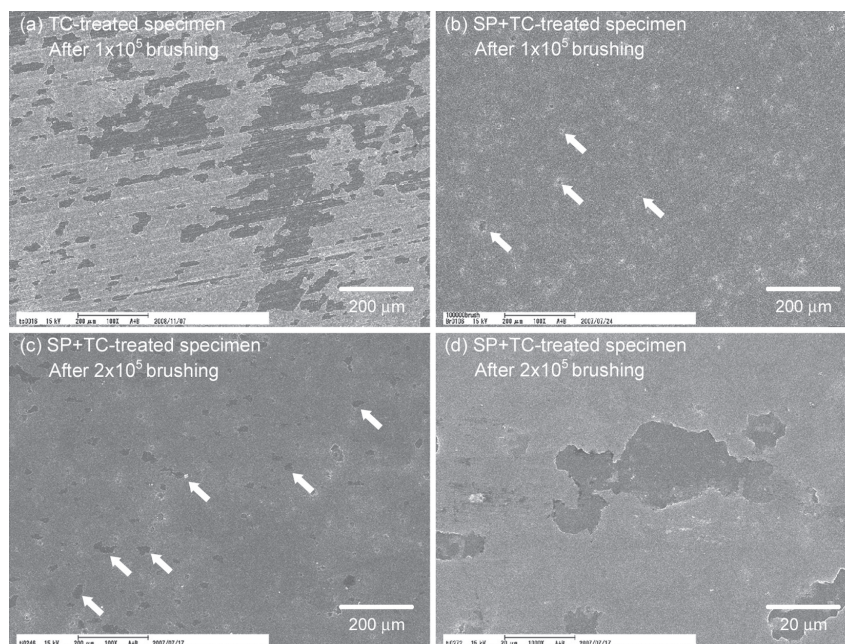


Fig. 6 SEM images of specimen surfaces after brushing. Arrows indicate defects on specimen. (a) TC-treated specimen after 1×10^5 brushing; (b) SP+TC-treated specimen after 1×10^5 brushing; (c) and (d): SP+TC-treated specimen after 2×10^5 brushing. SP: Siloxane primer. TC: TiO_2 coating

and 0.017 ± 0.013 , respectively. The statistical analysis revealed no significant difference in Ti/C ratio between at before brushing and at after 1×10^4 brushing ($p=0.09$), but a significant difference ($p=0.0001$) was observed between at before brushing or at 1×10^4 brushing and after 1×10^5 brushing cycles.

The Ti/C ratios in the SP+TC-treated specimens at before brushing, at after 1×10^5 brushing, and at 2×10^5 brushing were 0.027 ± 0.010 , 0.026 ± 0.009 and 0.021 ± 0.004 , respectively. No significant difference in Ti/C ratio was observed between at before brushing and at after 1×10^5 brushing. On the other hand, significant differences were observed in Ti/C ratio between at before brushing or at after 1×10^5 brushing and at after 2×10^5 brushing ($p=0.0001$).

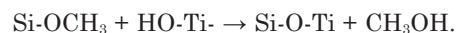
Figure 6 shows SEM images of the TC-treated and SP+TC-treated specimens at after brushing. At 1×10^5 brushing, the TC-treated specimens showed peeling at one layer from the surface (Figure 6(a)), whereas small defects were observed in parts of the surface of the SP+TC-treated specimens (Arrows shown in Figure 6(b)). At 2×10^5 brushing, defects of 20–40 μm in diameter size were observed in places (Figure 6(c)), and the number of defects increased with the increase of brushing cycles. The high magnification image of defect, as shown in Figure 6(d), was peeling at one layer from the surface. Figure 7 shows SEM and mapping images by EPMA analysis of Si, Ti and C obtained at after 2×10^5 brushing. In some areas where a lower concentration of Ti and Si was detected, there was pitting, with the bottom of the pits showing a higher concentration of C. The holes appeared as defects in the coated layers not only with TC treatment,

but also with SP treatment.

DISCUSSION

1. Coating of TiO_2 on PMMA substrates

The FT-IR spectrum revealed that SP treatment resulted in the creation of siloxane or silicate on the PMMA substrate. Acrylate groups in the acrylate-modified siloxane agent hydrophobically bonded with the PMMA substrate, siloxane groups were also detected at the surface layer coated with TiO_2 . In order to achieve chemical binding, a coated layer requires inorganic bonds:



The smooth surface of the SP+TC-treated specimens was achieved by homogenous coating. The TiO_2 coating, however, was very thin, or remained only in small patches, and crystal phase was not confirmed by XRD. The results of SEM and EPMA analysis revealed that application of an acrylate-modified siloxane agent yielded a rough surface and an approximately 2- μm thick layer on the PMMA substrate. An organic solvent of the siloxane agent such as acetone might have produced this rougher surface and layered structure. The rough surface created on the PMMA substrate was capable of facilitating mechanical bonding of the TiO_2 coating to the surface.

Application of TiO_2 to denture bases involves use of either composite created by addition of TiO_2 ²²⁾ and apatite to PMMA powder, or surface-coating with

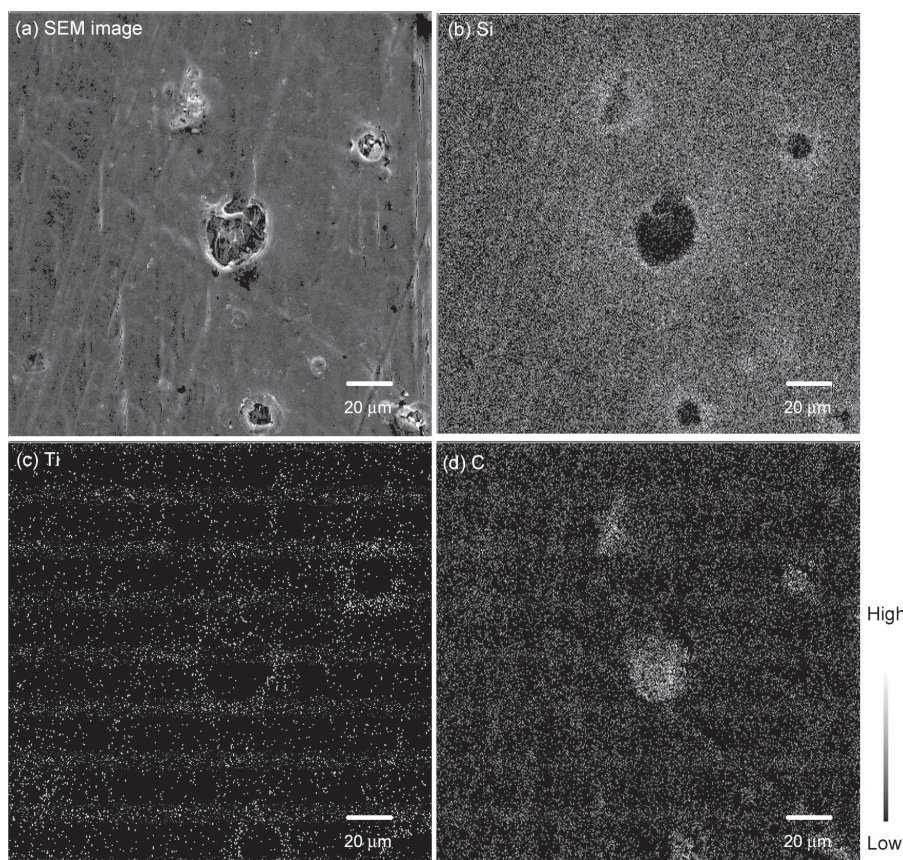


Fig. 7 EPMA mapping analysis of defective coating specimens (SP+TC) after 2×10^5 brushing. (a) SEM image, (b) Si, (c) Ti, (d) C. SP: Siloxane primer. TC: TiO_2 coating

TiO_2 ¹⁸⁾, as used in this study. Although the former method offers the advantage of semi-permanent antimicrobial and antifouling properties, mixing PMMA powder, which is an organic material, with TiO_2 , which is an inorganic material, may compromise the mechanical strength of the denture. On the other hand, surface coating with TiO_2 appears to exert a minimal influence on the mechanical strength of the whole denture, as the coating affects only the 2- μm upper surface of the denture base. Since the thickness of denture bases is more than 1 mm, their mechanical strength may not be compromised. Further study is needed to determine the relationships between thickness of coating and bonding strength to substrate and antibacterial effect, bearing in mind that thickness can be changed by concentration of sol or spray time¹⁹⁾.

2. Brush-wear durability of TiO_2 coating

The present study investigated the durability of a TiO_2 coating on a PMMA substrate against mechanical cleaning with a denture brush. The loading force of 300 gf and gliding speed of 150 cycles per 60 s were determined in a preliminary experiment by averaging the loading forces and gliding speeds applied by 5 healthy subjects during the cleaning of PMMA blocks. According to Harrison *et al.*, the typical brushing time

of a complete upper denture is 90 s per day²⁴⁾. Based on this, the 1×10^5 brushing cycle used in this study would correspond to more than approximately 1 yr of brushing.

The durability of the TiO_2 coating was evaluated by calculating the ratio of the amount of Ti, which comes from the TiO_2 coating, to the amount of C, which comes from the siloxane agent and PMMA substrate. A decrease in Ti/C ratio should indicate a loss of TiO_2 coating. The TC-treated specimens showed a decrease in Ti/C ratio after 1×10^5 brushing. On the other hand, in the SP+TC-treated specimens, a decrease in Ti/C ratio was seen at after 2×10^5 brushing. These results suggest that a TiO_2 coating on an SP treated-PMMA substrate can withstand at least 1×10^5 brushing. This indicates that a TiO_2 coating would offer sufficient durability in clinical application.

As shown in Figure 5, SEM after 1×10^5 brushing revealed peeling at one layer from the surface of the TC-treated specimens, and small cracks were observed in parts of the surface of the SP+TC-treated specimens. Additionally, small defect areas where the TiO_2 coating had become detached were observed in the SP+TC-treated specimens after 2×10^5 brushing. In such areas, little or no Si, and no Ti were detected (as shown in Figure 7), indicating that the bonding strength of the

TiO₂ coating might depend on the strength of the layer formed by SP treatment. This suggests that the acrylate-modified siloxane agent enhanced bonding of TiO₂ to the PMMA substrate through chemical, rather than mechanical, bonding.

The present study demonstrated that a TiO₂ coating on a PMMA substrate remained in place, even after mechanical stress consisting of 2×10⁵ brushing cycles. Defects in the TiO₂ coating were larger than the oral bacteria that cause denture plaque, as shown in Figures 6 and 7. However, it could be considered that antifouling and antibacterial properties would be maintained, as long as sufficient TiO₂ coating remained around the defect on the PMMA substrate. Since the method of TiO₂-coating used in this study is a simple technique, it would allow the surface to be re-coated without significantly altering the shape or mechanical properties of the denture itself.

CONCLUSIONS

The results demonstrate that a thin 2- μ m double-layer TiO₂ coating was obtained on a polymethyl methacrylate substrate by prior treatment with an acryloxypropyl trimethoxysilane-based agent, and that the durability of the TiO₂ coating was superior to that without prior treatment. These results suggest that application of an acrylate-modified agent enhances the durability of a TiO₂ coating in response to brushing.

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