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Color and gloss evaluation of titanium dioxide coating for acrylic resin denture base

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Abbreviated title: Color and gloss evaluation of TiO₂ coating for resin denture

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titanium dioxide, coating, primer
Abstract

Purpose: We examined the clinical appearance (color, gloss, and surface roughness) of TiO$_2$ coating on polymethyl methacrylate (PMMA) resin dentures.

Methods: A spraying method, using air brushes, was used to generate thin uniform TiO$_2$ coating. PMMA resin, primer-coated PMMA, and TiO$_2$-coated PMMA (with primer) specimens were compared.

Results: The Commission Internationale de l'Eclairage (CIE) color system revealed color variations between the with/without coated samples. The TiO$_2$-coated PMMA specimen displayed high levels of glossiness, highlighting the efficient self-cleansing actions of the denture. The measured surface roughness decreased upon primer coating, and increased following TiO$_2$ coating.

Conclusions: The thin TiO$_2$ coating afforded high levels of glossiness while maintaining the color of the denture base material.
1. Introduction

Acrylic resin is frequently used as a denture base material owing to its physical properties and esthetics [1]. However, acrylic resin degrades because of bacteria and fungi adhesion onto it [2,3], microbial invasion and colonization owing to water absorption [4], and surface roughening owing to mechanical and chemical cleaning [5]. Therefore, to improve the quality of the surface of resin, the titanium dioxide coating is used. The titanium dioxide coating on acrylic resin denture bases improves wettability, reduces adhesion of food bolus [6], and suppresses adhesion of bacteria and fungi [7]. We have reported that the use of a primer agent, which primarily consists of acryloxypropyl methoxysilane, for pre-treatment of the titanium dioxide coating affords durability of the titanium dioxide coating against brushing [8]. Moreover, the biocompatibility of a primer agent and TiO₂ coating agent has been already demonstrated [9].

To produce satisfactory dentures for patients, it is necessary to not only consider functionality, but also esthetic aspects [10,11]. Although self-cleansing action can be added by
titanium dioxide coating, there is a possibility that the color of dentures will change by white color of titanium dioxide materials. Furthermore, final polishing is not performed before the coating process to increase the surface area of coating; therefore, the surface is constant rough (Ra: about 0.3 µm). This may influence the esthetic features of dentures. Therefore, it is necessary to evaluate the clinical appearance of the titanium dioxide coating.

Rough surface of denture bases has no high level glossiness. However, the addition of glossiness has a positive influence on patients’ satisfaction. Regarding the self-cleansing action and esthetic features of denture base materials, although there are differences in the re-contouring and polishing work among clinicians and dental technicians depending on the methods used and clinical experience, these processes are generally time-consuming regardless of the type of polishing instrument [12,13]. The polishing of morphologically complicated denture areas is not regular; consequently, the self-cleansing action and esthetic features of denture bases deteriorate.
Furthermore, because the lubrication and glossiness of the surface acrylic resin denture base are lost during long-term use, it is difficult to retain good esthetic properties for a long period. Therefore, to simplify the manual process of denture polishing, to avoid long hours of dental laboratory work and to standardize products, surface glazing agents are used [14]. The characteristic requirements of surface glazing agents are lubrication and surface durability following treatment [15]. Furthermore, the surface glazing agent should not influence the color of the base material following application. So this coating material may also be able to be used as the surface glazing agent if it could afford the high levels of glossiness to dentures.

In this study, we investigate the influence of the titanium dioxide coating on the appearance of resin denture bases. We compare the color and degree of glossiness in the presence and absence of titanium dioxide coating.

2. Materials and methods

2.1. Plate specimens
Polymethyl methacrylate (PMMA) samples were prepared from wet-heat-curing acrylic resin (Acron, GC Corporation, Tokyo, Japan). The powder-to-liquid volume ratio was 1:0.43. The resulting mixture was packed into a plaster mold (18 mm in diameter, 1.0 mm in depth), and immersed in water at 60 °C for 60 min. (for primary polymerization) and then in boiling water for 60 min. (for secondary polymerization). Specimens were lapped up to the equivalent of grit #1000 using wet abrasive paper to make rough surface (Ra: about 0.3 μm).

2.2. TiO$_2$ coating

The PMMA specimens were pre-treated with a primer agent (Paltitan PTI5603S, Nihon Parkerizing, Kanagawa, Japan), of which the main component is acryloxypropyl trimethoxysilane in ethanol, that was sprayed for 2 sec. using an air-brush gun (Super Airbrush Advance, WAVE, Tokyo, Japan) connected with 0.6 MPa compressed air, then dried for 10 min. at 70 °C in air. TiO$_2$ coating agent (Paltitan PTI5603S, Nihon Parkerizing, Kanagawa, Japan), containing 2.0% anatase TiO$_2$ (5-10 nm in diameter) in water and ethanol, was then sprayed onto the
substrate for 2 sec. and dried in an oven for 10 min. at 70 °C. The specimens are denoted as PMMA, primer-coated PMMA, and TiO$_2$-coated PMMA (with primer). These specimens were sterilized with ethanol and stored in a dark room during one month until the experiment.

2.3. Measurements

The Commission Internationale de l'Eclairage (CIE) $L^*a^*b^*$ values were obtained using a reflective colorimeter (Shade Eye NCC, Shofu, Kyoto, Japan). All measurements were performed in triplicate with blocking out light on a black back ground. The measurement range was 3mm in diameter. The number of specimens used per measurement was five ($n = 5$) and the means of $L^*$, $a^*$, and $b^*$ were calculated. $\Delta E^{*ab}$ was calculated using the formula $\Delta E^{*ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where $\Delta E^{*ab}$ represents the color difference, and $\Delta L^*$, $\Delta a^*$, and $\Delta b^*$ represent differences in lightness, red–green scale color, and yellow–blue scale color, respectively [16]. Because the color system can be used as a color transfer standard with absolute color scales, the use of a control for comparison for each
measurement is unnecessary. Thus, the color system is suitable for the evaluation of the different specimens in this study. Furthermore, $\Delta E_{ab}$ can be used as an index to evaluate color differences when digitized colors are compared; when $\Delta E_{ab}$ is large, color differences become clear.

The glossiness of each specimen was measured with a glossmeter (IG-331, Horiba, Tokyo, Japan) at an angle of 60° from the surface normal with blocking out light on a black background. The measurement range was 3×6mm ellipse. Three measurements were obtained at different directions on each specimen. The number of specimens used per measurement was five ($n = 5$) and the mean glossiness was calculated to analyze.

The surface roughness of each specimen was measured with a profilometer (Surfcom 130A, Tokyo Seimitsu Co., Tokyo, Japan) using a tracing length of 4 mm and a cut-off value of 0.8 mm. Five tracings were recorded at different locations on each specimen. The number of specimens used per measurement was five ($n = 5$) and the mean roughness ($R_a$) was calculated to
analyze.

The surface morphology was assessed using field-emission scanning electron microscopy (SEM) on a scanning electron microscope (SU6600, Hitachi, Tokyo, Japan).

2.4. Statistical analysis

One-way ANOVA with Bonferroni multiple comparison was used to examine differences between the three specimen groups; $p < 0.05$ was considered statistically significant.

3. Results

Figure 1 shows the color data of each specimen. The means of the $L^*$, $a^*$, and $b^*$ values of PMMA were $50.27 \pm 0.62$, $21.01 \pm 0.37$, and $11.77 \pm 0.32$, respectively. The primer-coated specimen featured $L^*$, $a^*$, and $b^*$ means of $50.17 \pm 0.73$, $21.31 \pm 0.47$, and $12.07 \pm 0.43$, respectively. The TiO$_2$-coated specimen featured $L^*$, $a^*$, and $b^*$ of $50.61 \pm 0.39$, $20.33 \pm 0.36$, and $11.09 \pm 0.46$, respectively. There were significant differences between the primer-coated and TiO$_2$-coated specimens in terms of the $a^*$ and $b^*$ values. The obtained $\Delta E^*ab$ values between PMMA and
primer-coated, between primer-coated and TiO$_2$-coated, and between PMMA and TiO$_2$-coated specimens were 0.43, 1.45 and 1.02, respectively.

Figure 2 shows the results of the glossiness measurements. The glossiness levels of the PMMA, primer-coated, and TiO$_2$-coated specimens were $3.06 \pm 0.89$, $8.60 \pm 0.68$, and $12.8 \pm 0.73$, respectively. There were significant differences between the PMMA and primer-coated, primer-coated and TiO$_2$-coated, and PMMA and TiO$_2$-coated specimens.

Figure 3 shows the surface roughness of each specimen. The surface roughness levels of the PMMA, primer-coated, and TiO$_2$-coated specimens were $0.30 \pm 0.02$, $0.29 \pm 0.00$, and $0.35 \pm 0.01 \mu$m, respectively. There were significant differences between the primer-coated and TiO$_2$-coated, and PMMA and TiO$_2$-coated specimens.

Figure 4 shows the SEM images of the surface morphology of the specimens at two magnifications: 100× and 5000×.

4. Discussion
Two methods have been proposed for the application of titanium dioxide on denture materials: titanium dioxide is either added or coated on the base material. Regardless of the method employed, titanium dioxide, which has photocatalytic properties, is white. However, the amount of added/coated titanium dioxide influences the color. Regarding the amounts of TiO₂, added amounts above 5 wt.% are necessary to achieve photocatalytic effects [17]. Coating of titanium dioxide at increasing concentrations might result in thicker layers that not only influence the mechanical characteristics, but also the color of the denture base. The results showed significant differences in $a^*$ and $b^*$ between the primer-coated and TiO₂-coated samples. However, because no significant differences in $a^*$ and $b^*$ were noted between the PMMA and primer-coated samples, and between the PMMA and TiO₂-coated samples, color changes were considered to be absent. Furthermore, $\Delta E^{*ab}$ was lower than 3, thus color differences were considered to be below the level of macroscopic discrimination. Generally, when $\Delta E^{*ab}$ is lower than 3, macroscopic discrimination of color differences is
difficult [18]. This was believed to be due to the thin layer coating and the small amount of titanium dioxide employed.

Currently, there are no existing standards on glossiness for dentures. Several methods are available to measure the degree of glossiness. In this study, optical reflection measurements were performed at 60°, which is considered the most suitable for resin denture base materials [19]. Surface lubrication greatly influences surface glossiness. Typically, the degree of glossiness increases with increasing lubrication of the material surface. Increases in the glossiness using surface glazing agents increase the thickness of the material coating and surface lubrication. In contrast, this spraying method for coating using air brushes produces thin coatings. Coatings could change the surface morphology of base materials, even if their layer are thin. SEM observation revealed that coating on the entire material surface was achieved, and the original surface morphology remained unchanged by low magnification. Therefore, there is a possibility that the surface does not exhibit
lubricating properties, and that glossiness does not increase. However, the results in the present study revealed that even thin layers promote higher degrees of glossiness. This suggests that the dental laboratory work relating to polishing can be decreased and the denture surface can be standardized.

The results of this study showed that primary coating did not lead to increase in the surface roughness, and the surface did not become rough. In contrast, titanium dioxide coating increased the surface roughness of about 0.05 \( \mu \text{m} \). It is known that microbial adhesion increases with increases in the surface roughness of resin denture base [20,21]. However, it has additionally been reported that there is no correlation between the surface roughness and microbial adhesion [22]. It has already reported that this coating has effects to suppress microbial adhesion [7]. Based on these information, surface hydrophilicity of this coating may affect the suppressing effect of microbial adhesion against increasing of surface roughness. As determined from SEM analysis, the coating material was observed in the hollow and fissured areas of the acrylic resin,
suggesting that invasion of bacteria and external deposits can be prevented from a microscopic perspective.

The titanium dioxide coating used in this study was not dislodged, even under the application of 100,000 brushes on equal terms with brushing a maxillary denture at 300 gf for 90 sec. per day for one year [8]. Based on this finding, we conclude showed that this titanium dioxide coating has sufficient durability under conditions associated with the long term use of dentures.

This application of titanium dioxide coatings not only improves the self-cleansing action of dentures, but also increases the surface glossiness without influencing the color of the base material.

5. Conclusions

The titanium dioxide coating on denture base materials was achieved; the thin coating increased the degree of surface glossiness, while maintaining the color of the resin denture base.
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Conflict of interest

There are no conflicts of interest with regard to this study.
References


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Figures

Figure 1. Color values

Color measurements of the PMMA, primer-coated, and TiO$_2$-coated specimens using the $L^*a^*b^*$ color system. No significant differences in $L^*$, $a^*$, and $b^*$ were noted between the PMMA and TiO$_2$-coated specimens.
Figure 2. Surface glossiness

Glossiness measurements of the PMMA, primer-coated, and TiO$_2$-coated specimens. The reflectance of the surface was digitized with the angle of incidence of light set at 60°. The degree of glossiness increased in the presence of coating.

\[ p<.05, \ n=5 \]
Figure 3. Surface roughness

Roughness measurements of the PMMA, primer-coated, and TiO$_2$-coated specimens. The average roughness ($R_a$) values are reported. The roughness increased in the presence of titanium dioxide coating.

![Bar chart showing surface roughness measurements for PMMA, primer-coated, and TiO$_2$-coated specimens.](image)

* $p<.05$, $n=5$
Figure 4. Surface observation

Megascopic surface of specimens and surface observation of specimens by SEM at respective magnifications of 100× and 5000×: (A, B, C) PMMA polished up to an equivalent of grit #1000; (D, E, F) primer-coated PMMA; and (G, H, I) TiO$_2$-coated PMMA. No significant differences in the surface morphology were observed at 100×. However, at a magnification of 5000×, PMMA showed the highest surface concavo-convexity. The primer agent was observed in the concavo-convex areas, and the surface displayed a lubricating morphology. Furthermore, titanium dioxide particles were scattered across the surface of the TiO$_2$-coated specimen.