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치과용 시멘트와의 결합강도를 향상시키기 위한 폴리도파민 코팅 티타늄의 효과

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〈Abstract〉

Efficacy of polydopamine-coated titanium in order to improve bond strengths for dental resin cement

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이 연구의 목적은 폴리도파민이 코팅된 티타늄 표면의 특성을 확인하고 치과용 레진 시멘트의 전단 결합 강도에 미치는 영향을 조사하는 것이다. pH 8.5의 10 mM Tris-HCl 완충액에 2 mg/mL 도파민을 첨가하여 만든 폴리도파민 용액에 티타늄 시편을 24시간 동안 침지하여 폴리도파민을 표면에 코팅 하였다. 폴리도파민이 코팅된 티타늄 시편의 표면 특성은 X선 광전자 분광법(XPS), 주사 전자 현미경(SEM) 및 접촉각 측정(contact angle)에 의해 관찰되었다. 그리고 치과용 레진 시멘트와의 결합 강도는 전단 접착 강도 모드 하에서 평가되었다. 폴리도파민이 코팅된 티타늄 시편의 표면을 XPS로 분석한 결과, 티타늄 표면으로부터 Ti2p 피크가 나타나지 않았고, 시편 표면의 미세 구조에서는 코팅 후 나노 미터 크기의 폴리도파민 입자가 시편 표면에 전체적으로 분포되어 있음을 보여 주었다. 또한 폴리도파민이 코팅 된 티타늄 시편의 접촉각은 코팅이 되지 않은 티타늄 시편보다 작은 접촉각으로 폴리도파민 코팅에 의해 시편 표면의 젖음성이 증가하였음을 나타내었고, 티타늄 표면에 폴리도파민이 성공적으로 코팅이 되었음을 확인 할 수 있었다. 그리고 폴리도파민이 코팅 된 티타늄 시편의 레진 시멘트와의 전단 결합 강도는 코팅되지 않은 티타늄 시편보다 증가한 것을 확인하였다. 이 결과는 폴리도파민을 이용한 티타늄의 표면 처리가 티타늄에 대한 시멘트의 결합 강도를 향상시킬 수 있는 효과적인 표면 조건을 제공한다는 것을 나타낸다.

주제어: 폴리도파민, 티타늄, 전단결합강도, 젖음성, 레진 시멘트

Ⅰ. INTRODUCTION

Titanium is popular in dentistry as a substitute material for the noble and non-noble alloys because of its superior biocompatibility, good mechanical properties and high corrosion resistance (Francescantonio et al., 2012; Al-Helou, 2014; Ramesh et al., 2016). Prostheses with titanium have been indicated for a metallic framework in fixed partial denture, full crowns, prostheses with multiple units, adhesive prostheses, root posts and framework for dentures (Schneider et al., 2007).

Although titanium has many advantages, there are concerns regarding the weak bonding between luting materials and cast titanium when luting cements are indicated (Kılıçarslan et al., 2016). Many types of

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surface treatment have been proposed to improve the bond strength of titanium to cement. These treatments include sandblasting, silica coating, acid etching, and use of functional monomers (Veljee et al., 2015). However, the problems of achieving a durable and predictable bond between titanium and luting material still remain. Hence the development of surface modification is a real essential.

Recently, the adhesive strategies of the marine mussel adhesive proteins have attracted great attention owing to the amazing ability of mussels to adhere to various kinds of surfaces (Li et al., 2014). Natural adhesive proteins are found in the byssus threads of mussels, which they use to adhere to the surfaces of wet solids such as rocks to allow them to remain anchored despite strong waves. Mussel-inspired proteins have more adhesive potential than synthetic adhesives, as they have excellent tensile strength and flexibility. Mussel-inspired proteins can adhere to various surfaces such as glass, metal, plastics, and biological materials (Lee et al., 2014). Thus, this represents a very convenient and universal method for adding an organic layer to various materials including polymers, metals, and ceramics (Kang et al., 2013).

The current study was concerned with the bonding of resin cement to titanium surface and how we could improve the bond strength at the cement-titanium junction. Previous studies (Ho et al., 2015; Veljee et al., 2015) have used mechanical surface treatments to increase the bond strength at the cement-titanium interface, but there are no studies, which have used of polydopamine coating treatments. Hence, the aim of this in vitro study was to use polydopamine coating treatment to increase the shear bond strength at the cement-titanium interface reducing the chances of failure of the prosthesis.

II. MATERIALS AND METHODS

Dopamine hydrochloride and Tris-HCl buffer were supplied by Sigma-Aldrich (USA). Ti6Al4V titanium alloy plates (diameter 10 mm × thickness 3 mm) were chosen as the substrates for modification.

The resin-based cements tested in this study are summarized in Table 1.

1. Poly-dopamine coating on titanium alloy plates

Commercially available titanium alloy (Ti6Al4V) disks were used as substrates in this study. These disks were polished by #800 sandpaper and ultrasonically cleaned using acetone, ethanol and distilled water, respectively. To prepare the polydopamine coating solution, dopamine was dissolved at a concentration of 2 mg/mL in 10 mM Tris-HCl (pH=8.5). The titanium disks were immersed in the dopamine solution for 24 h at room temperature. The

Table 1. Materials used in the present study

Brand name	Manufacturer	Composition* (batch number)	Filler loading/ average particle size*
RelyX U200 (dure-cured)	3M ESPE, Seefeld, Germany	Base: Mono-, di- and tri-glycerol esters of phosphoric acid dimethacrylate, triethylene glycol dimethacrylate (TEGDMA), glass, silica, sodium persulfate, tert-butyl peroxy-3,5,5-trimethylhexanoate; Catalyst: substituted dimethacrylate, 1,12-dodecane dimethacrylate, glass, silica, calcium hydroxide, calcium salt of 1-benzyl-5-phenyl-barbic-acid, sodium *p*-toluenesulfinate (574751)	43 vol%/12.5 μm

dopamine-coated titanium substrates were washed with distilled water and air dried at room temperature (Yu et al., 2013; Lee et al., 2014).

2. Surface characteristics analysis

The surface composition of coated surface was analyzed using X-ray photoelectron spectroscopy (XPS). The XPS survey spectra were obtained using pass energy of 100 eV and energy step size of 1 eV, and the high resolution XPS spectra data were collected using pass energy of 50 eV and energy step size of 0.1 eV. All binding energies were referred to the C1s neutral carbon peak at 284.6 eV. To determine the morphological microstructure of the coated layer, the specimens were sputter-coated with platinum, followed by analysis using a scanning electron microscope (SEM, JSM-6700F, Jeol, Japan).

The wettability of the polydopamine-coated titanium plate was investigated by the water contact angle measurement. Static water contact angle was measured by sessile drop technique. Micro-syringe was filled with distilled water and placed in the clamp of micromanipulator. After 5 s of 10 μL water droplet addition, water contact angle was measured on each titanium surface and analyzed using the software supplied by manufacturer. All measurements were performed at room temperature.

3. Shear bond strength test

When we performed the shear bond strength test, we used the method developed by custom-manufactured bonding jig. The specimens were placed in a specially fabricated bonding device with a cylindrical Teflon jig of 2.38 mm inner diameter and 3 mm in height. Dual-cure resin cement was condensed into a Teflon jig and cured for 40 s according to the manufacturer's instructions. After the cement had polymerized using light curing (Bluephase 20i, Ivoclar Vivadent, Schaan, Liechtenstein), the jig was disassembled. Until the shear bond strength test, all bonded specimens were stored in a water bath at 37 °C for 24 h. For de-bonding, the specimens were engaged perpendicularly at their bonded resin cylinder bases with a round-notched custom shear blade in a universal testing machine (3366, Instron Inc., USA) at a crosshead speed of 0.5 mm/min and a 1 N load cell (Lee et al., 2015).

Ⅲ. RESULTS

1. Polymerization of polydopamine

When titanium plate was treated with dopamine, the surface turned brown at pH 8.5 (Fig. 1).

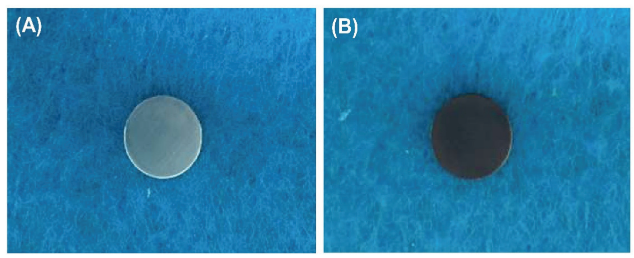

Figure 1. Changes in the color of dopamine upon polymerization to polydopamine according to immersion method: (A) non-coated titanium plate, (B) polydopamine-coated titanium plate.

2. Surface characteristics of the specimens

The chemical composition differences of the titanium sample before and after treatment were analyzed by XPS. Fig. 2 shows the wide scan spectra of XPS for the two treated surfaces in this study: non-coated titanium and polydopamine-coated titanium. Compared to non-coted titanium surface, C, O and N peaks were also observed but Ti2p peaks disappeared on the polydopamine-coated titanium surface. The polydopamine-coated titanium spectra indicate that a homogeneous dopamine coating was formed and fully covered titanium surface.

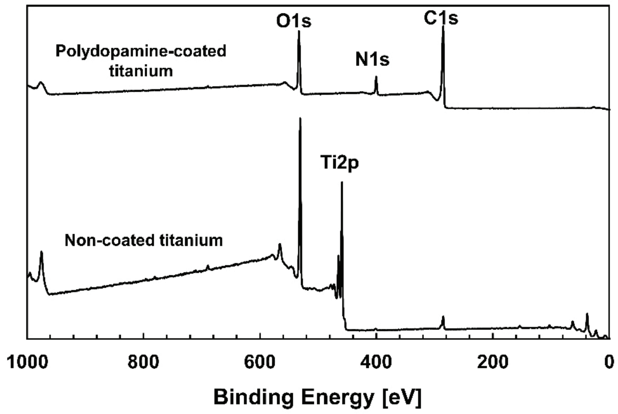

Figure 2. Typical XPS survey spectra of titanium surfaces studied: non-coated titanium surface and polydopamine-coated titanium surface.

Fig. 3 shows images of non-coated titanium and polydopamine-coated titanium surface. In the non-coated titanium specimen, no obvious microstructures were observed. On the other hand, the microstructural features of the polydopamine coatings revealed that nanometer-sized bright granules were randomly distributed after coating.

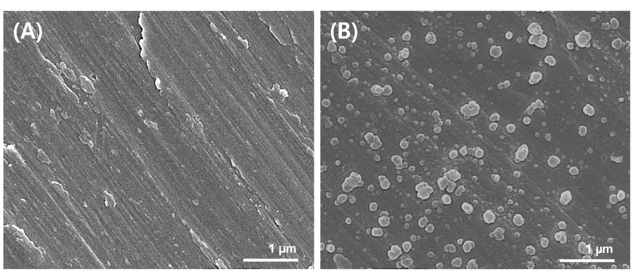

Figure 3. Scanning electron microscopy images of the non-coated titanium plate (A) and the polydopamine-coated titanium plate (B) (original magnification 20,000×).

A photo of the measured contact angle is shown in Fig. 4. The measured contact angle was 82.16° for the non-coated titanium specimen (Fig. 4(A)), but it was reduced to 38.28° in the polydopamine-coated titanium specimen (Fig. 4(B)), indicating that the latter specimen was more hydrophilic than the non-coated titanium specimen.

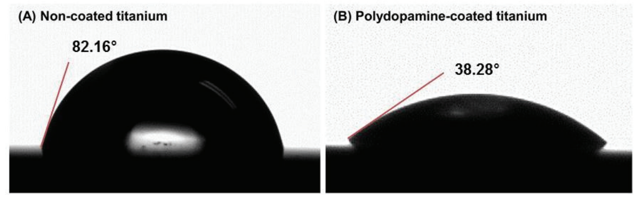

Figure 4. Contact angles of the non-coated titanium surface (A) and the polydopamine-coated titanium surface (B).

3. Comparison of shear bond strength values

Table 2 summarizes the shear bond strength for the experimental groups. The resin cement shear bond strength values of polydopamine-coated titanium plate (13.38 MPa) was higher than the non-coated titanium plate (5.05 MPa) ($p<0.05$).

Table 2. Shear bond strength values in MPa of resin cements to titanium (n=15)

Test groups	Mean (SD)
Non-coated titanium	5.05 (1.32)
Polydopamine-coated titanium	13.38 (3.32)

Ⅳ. DISCUSSIONS

The strong bonding between titanium and resin plays an important role in the longevity of prosthesis. When titanium is used for a metallic substructure for restoration covered with resin with weak bond strength between layers, micro-leakage tends to appear on the metal-resin interface leading to failure of prosthodontic prostheses (Lee et al., 2009). To overcome these defects, sandblasting, electrolytic etching technique and chemical etching technique are used to obtain a micro-roughness on the metals. However, micro-leakage cannot be solved completely because all the techniques are based on mechanical bonding (Lee et al., 2009).

To solve the problem, pH-induced polymerization of dopamine have been introduced for surface modification (Lee et al., 2007).

Dopamine, which was inspired by the composition of adhesive proteins in mussels, was reported to form thin, surface-adherent polymer films onto virtually all material surfaces, in alkaline aqueous media. Only by a simple immersion of substrate in a dilute aqueous solution of dopamine, buffered to alkaline pH, could result in spontaneous deposition of a thin polydopamine film (Jiang et al., 2014). It has been widely used to prepare a variety of ad-layers, including self-assembled monolayers through deposition of long-chain molecular building blocks, multilayer films, surface modification of the inorganic materials, nano-capsules for drug delivery and bio-inert and bioactive surfaces via grafting of macromolecules (Wei et al., 2010).

Dopamine polymerization results in the formation of quinones by catechol oxidation or alkaline pH-induced oxidation. Quinones and their derivatives are highly chemically reactive; they are continuously oxidized, polymerized, or condensed via non-enzymatic processes, and are then processed by enzymes involved in melanin pigmentation (Jiang et al., 2014; Lee et al., 2014). The change in color of dopamine from light violet to dark green due to dopamine polymerization is shown in Fig. 1.

The formation of polydopamine coating on titanium has been confirmed by XPS analyses of the materials surfaces (Fig. 2). The absence of Ti2p peak from polydopamine-coated titanium surface indicates that the polydopamine coating completely has covered the titanium surface. More importantly, polydopamine coating exhibits strong reactivity towards various nucleophiles with amine and thiol groups due to the presence of quinone after polymerization. Thus, titanium surface containing large amounts of amine and thiol groups have been successfully conjugated through polydopamine coating for various applications, such as adhesion properties (Yu et al., 2013). In addition, when we analyzed the composition of the specimens using SEM, we observed irregularly-shaped polydopamine particles on the surfaces of the specimens coated with polydopamine.

When wettability was measured by adding water to the titanium specimens (Fig. 4), the contact angle of the polydopamine-coated specimen was 38.28°, lower than that of the non-coated titanium specimen. Lee et al., (2014) reported that increased wettability and decreased contact angle indicated a hydrophilic surface with a high surface energy, an excellent environment for adhesion properties (Yang et al., 2015). The surface contact angle has been recognized as one of the most governing and influencing parameters to control the bond characteristics, particularly the bond strengths, and the smaller the contact angle the higher the surface bond strength. Moreover, with a smaller contact angle, the bonding agent can penetrate easily into surface convex portions, resulting in a strengthening of the bond (Yoshida et al., 2005; Yang and Zhao, 2011). In this study, we observed that the specimens that underwent surface treatment had better wettability and stimulated greater shear bond strength than the non-modified specimens, which could result in increased adhesion properties of a material (Kang et al., 2013; Lee et al., 2015). Therefore, the approach described here may represent an enabling strategy to improve the performances of titanium by surface modification.

Ⅴ. CONCLUSION

In summary, polydopamine-coated titanium was successfully prepared from a dopamine solution in 10 mM Tris-HCl buffer solution at pH 8.5. The formation of polydopamine coating on titanium has been confirmed by XPS analyses of the materials surfaces. The absence of Ti2p peak from polydopamine-coated titanium surface indicates that the polydopamine coating completely has covered the titanium surface. Using SEM, we determined that nanometer-sized bright granules were randomly distributed after coating. The static contact angles on non-coated titanium and polydopamine-coated titanium surfaces were 82.16° and 38.28°, respectively. Therefore, the findings from our research suggest that polydopamine coating results in greater hydrophilicity of titanium surface and enhancement of adhesion properties.

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ABSTRACT

Efficacy of polydopamine-coated titanium in order to improve bond strengths for dental resin cement

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This study investigated the effects polydopamine-coated titanium surfaces on resin cement shear bond strengths, and characterized polydopamine-coated titanium surfaces. Polydopamine was coated onto the titanium surfaces by immersion in a 2 mg/mL dopamine solution in 10 mM Tris-HCl buffer at pH 8.5. The surface characteristics of polydopamine-coated titanium plates were observed by X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and contact angle measurements. And then, the resin cement bond strengths were evaluated under shear bond strength mode. The formation of polydopamine coating on titanium has been confirmed by XPS analyses of the materials surfaces. The absence of Ti2p peak from polydopamine-coated titanium surface indicates that the polydopamine coating completely has covered the titanium surface. Microstructural features revealed that nanometer-sized bright granules were randomly distributed after coating. The cement shear bond strength of polydopamine-coated titanium plate was higher than the non-coated titanium plates ($p<0.05$). The more surface wetted with the cement material, the higher the resultant shear bond strength value. As a results, bond strengths are correlated to wettability. These results suggest that a treatment of polydopamine surface provides an effective surface condition to enhance the cement bond strength to titanium.

Key Words: Polydopamine, titanium, shear bond strength, wettability, resin cement