

Effect of 4-MET- and 10-MDP-based Primers on Resin Bonding to Titanium

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The purpose of this study was to investigate the effect of a 4-MET- and 10-MDP-based primer on the bond strength of two resin cements (SuperBond C&B, Sun Medical; Panavia Fluoro Cement, Kuraray) to titanium (Ti). Ti plates were treated with six experimental primers consisting of, respectively, 10-MDP and 4-MET in concentrations of 0.1, 1 and 10wt%, or were kept untreated (control). The highest tensile bond strength of Panavia Fluoro Cement to Ti was obtained when the Ti surface was pre-treated with 10wt% 10-MDP and was significantly higher than that when a lower concentrated 10-MDP-based primer or any 4-MET-based primer was used. On the contrary, no significant difference in tensile bond strength of SuperBond C&B was found for the untreated and six pre-treated Ti surfaces, although pre-treatment with each 10-MDP-based primer resulted in a higher tensile bond strength as compared to any 4-MET pre-treatment. Altogether, the data obtained strongly suggest that 10-MDP is effective to improve the adhesive performance of resin to titanium.

Key words: Titanium; 10-MDP; 4-MET

INTRODUCTION

Titanium (Ti) and its alloy have been widely employed as implantable materials in dentistry and orthopedics, mainly because of their osseointegrative properties, their excellent biocompatibility and high resistance to corrosion. Titanium also possesses several advantages as a prosthetic material, such as excellent biocompatibility, good mechanical properties and low density^{1,2}. In order to facilitate the fabrication of prosthetic devices from pure Ti and/or its alloys, many researchers have been working to develop new Ti casting technologies. For instance, specially adapted investment materials have been developed to improve the castability of Ti alloys³⁻⁶. In addition, research has been conducted to improve the machinability of Ti blocks so that Ti and/or Ti alloy prosthetic devices can be fabricated using dental CAD/CAM systems⁷⁻⁹.

Indirect Ti restorations are commonly luted with composite cements. Bonding of resin to titanium has been improved during the past decades and several techniques have been developed in an attempt to achieve more stable bonding. Adhesion of resin to a substrate depends on both micromechanical interlocking and physico-chemical bonding¹⁰. Although some resins have a potential to adhere physico-chemically

to substrates, micromechanical interlocking to the inner surface of the restoration is often the primary mechanism bonding is based upon¹¹. Clinically, sandblasting Ti with aluminum oxide is commonly employed for surface cleaning and to achieve a proper micro-retentive topography, resulting in an immediate increase in bond strength. With the increasing demand for prosthetic devices fabricated out of Ti, much effort has been invested to develop resin adhesives that bond effectively to Ti. Several ways to pre-treat Ti have been introduced, such as the use of adhesion-promoting monomers. Kibayashi *et al.* reported that the bond strength to pure Ti was higher than to untreated Ti after being exposed to plasma in air or in CO₂ gas atmosphere¹². Ban reported that the bond strength of resin to pure Ti and its alloys increased after alkaline treatment^{13,14}. Unfortunately, although several of these methods effectively improve the adhesive properties of resin to Ti, they are rather complicated and time-consuming so that they have hardly been accepted for routine use in clinical practice. The purpose of this study was to investigate the effect pre-treating Ti with two monomer-based primers as part of an adhesive luting procedure or resin-veneering procedure, may have on the bond strength.

MATERIAL AND METHODS

Pre-treatment of Ti surface

Commercially available pure Ti plates (Grade-II; Kobe Steel, Ltd., 10×10 mm, 3 mm thick) were used in this study. The surface of the Ti plates was ground on a 600-grit silicon carbide paper, followed by ultrasonic cleaning in ethanol for 5 min. The Ti plates were then pre-treated with six different experimental primers consisting of 10-methacryloxydecyl dihydrogen phosphate (10-MDP) and 4-methacryloxyethyl trimellitic acid (4-MET) in concentrations of 0.1, 1 and 10wt% (in 50wt% ethanol) for 5 min at room temperature (Fig. 1). As a control, additional Ti plates were kept untreated after grinding and ultrasonic cleaning.

Tensile bond strength

A stainless steel rod (7 mm in diameter, 20 mm in length) was luted onto the treated and untreated Ti plates using two luting composites, SuperBond C&B (Sun Medical, Moriyama, Japan) and Panavia Fluoro Cement (Kuraray, Tokyo, Japan), strictly according to the manufacturer's instruction. For the control (untreated Ti), SuperBond C&B was applied following both the so-called brush-dip technique as well as the bulk-mix technique. The specimens were left undisturbed for 15 min and then stored in water at 37 °C for 24 h. The tensile bond strength was determined using a universal testing machine (AGS-1000A, Shimadzu Co., Kyoto, Japan) at a crosshead speed of 1 mm/min. Ten specimens were tested for each group. Data were analyzed by one-way analysis of variance (ANOVA). When the F-ratios were significant ($p < 0.05$), Scheffe's multiple comparison test was used to compare mean values at $p < 0.05$. After tensile testing, the fractured surfaces were examined using a magnification glass (10×) to evaluate the modes of failure. The failure modes were classified into 'adhesive failure at the resin-metal interface',

'cohesive failure within the luting composite' or as 'mixed' in case the former two modes occurred together.

RESULTS

The tensile bond strength of Panavia Fluoro Cement and SuperBond C&B applied following the bulk-mix and brush-dip technique to untreated Ti (control) is graphically presented in Fig. 2. The tensile bond strength of SuperBond C&B to Ti using the bulk-mix technique was significantly higher than that of Panavia Fluoro Cement and that of SuperBond C&B applied following the brush-dip technique.

Fig. 3 shows fractured Ti surfaces after tensile bond strength testing. All specimens of SuperBond C&B applied following the brush-dip technique showed a mixed failure pattern. On the contrary, failures commonly occurred cohesively in the SuperBond C&B luting cement, when it was applied following the bulk-mix technique.

The tensile bond strength of SuperBond C&B to untreated Ti (control) and Ti treated with either 10-MDP or 4-MET in concentrations of 0.1, 1 and 10wt% is shown in Fig. 4. No significant difference in tensile bond strength was determined for the untreated and six treated Ti surfaces. However, a tendency existed to result in higher tensile bond strength when Ti was pre-treated with 10-MDP than with 4-MET, irrespective of the respective monomer concentration.

Fig. 5 shows the tensile bond strength of Panavia Fluoro Cement to untreated Ti (control) and Ti treated with either 10-MDP or 4-MET in concentrations of 0.1, 1 and 10wt%. The highest tensile bond strength of Panavia Fluoro Cement to Ti was obtained when Ti was pre-treated with 10wt% 10-MDP, and was significantly higher than when Ti was treated with either 0.1wt% 10-MDP or 0.1, 1 or 10wt% 4-MET. Actually, 10-MDP improved the ten-

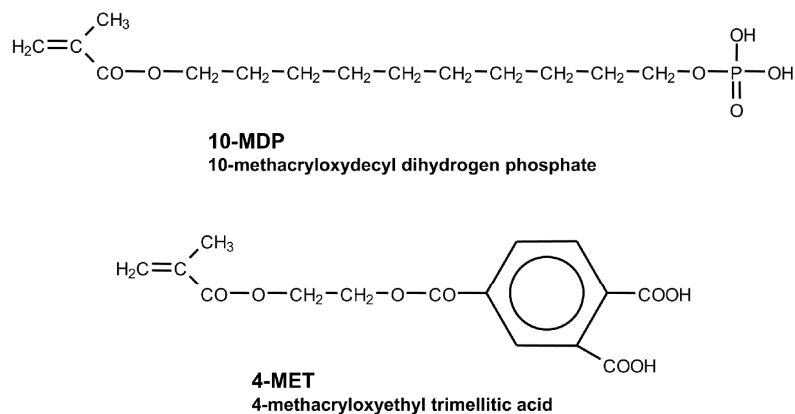


Fig. 1 Chemical structure of 10-methacryloxydecyl dihydrogen phosphate (10-MDP) and 4-methacryloxyethyl trimellitic acid (4-MET).

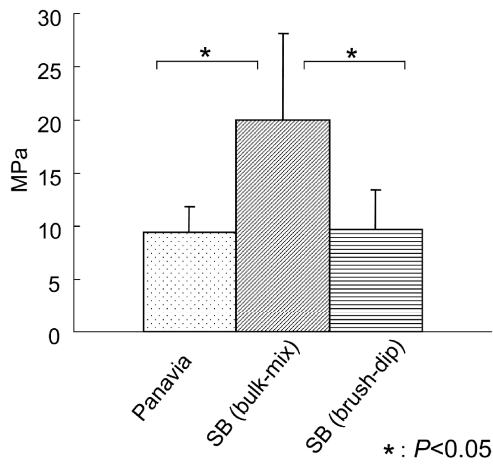


Fig. 2 Tensile bond strength to untreated Ti (control) of Panavia Fluoro Cement and SuperBond C&B applied either following the bulk-mix and the brush-dip technique.

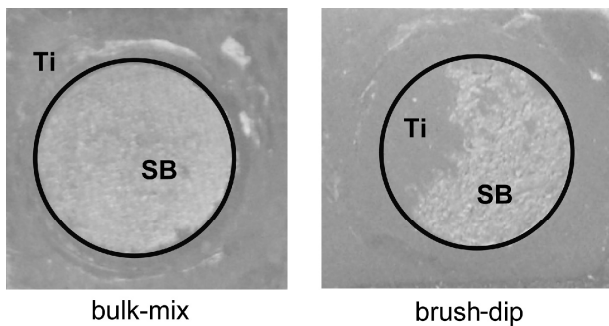


Fig. 3 Tensile bond strength fractured surfaces of SuperBond C&B applied to untreated Ti (control) following the bulk-mix and the brush-dip technique. SB: SuperBond C&B.

sile bond strength of Panavia Fluoro Cement to Ti in a dose-dependent manner. When Panavia Fluoro Cement was bonded to Ti, fractures never occurred adhesively at the resin-stainless steel rod interface or cohesively within the luting composite. All specimens of all 7 groups showed a mixed failure pattern.

DISCUSSION

Today, gold alloys are still mainly used for fixed prostheses, although these noble alloys are rather costly. In order to reduce costs for fixed prostheses, Ti and its alloys are expected to substitute noble alloys, because Ti as the fourth-most available structural metal in the earth's crust (following aluminum, iron, and magnesium)¹⁵, is much cheaper, while being equally biocompatible as gold. Titanium is nowadays already more often used to replace noble

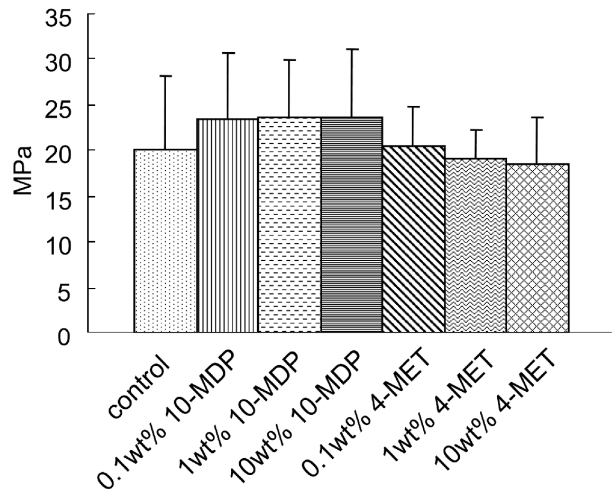


Fig. 4 Tensile bond strength of SuperBond C&B to untreated Ti (control) and to Ti treated with either 10-MDP or 4-MET in concentrations of 0.1, 1 and 10wt%.

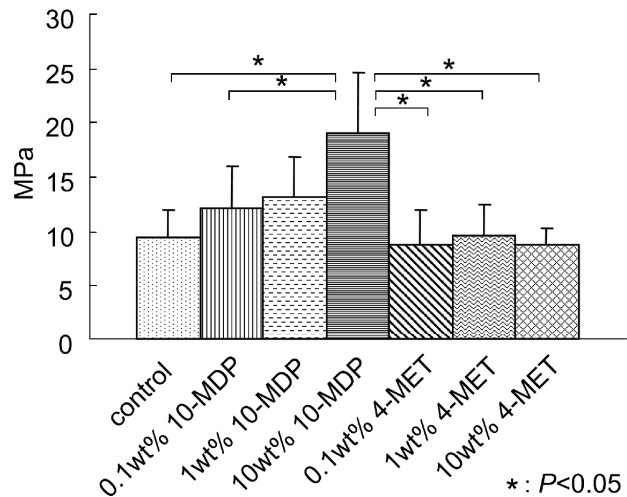


Fig. 5 Tensile bond strength of Panavia Fluoro Cement to untreated Ti (control) and to Ti treated with either 10-MDP or 4-MET in concentrations of 0.1, 1 and 10wt%.

alloys in prosthetic applications in case of allergy to the latter metal alloys¹⁶. Also in order to avoid intra-oral galvanic effects, Ti and its alloys are preferred to serve as implant abutments and supra-structures¹⁷, because Ti and its alloys are generally also used as dental implant fixture material.

In this study, we investigated the effect of 10-MDP and 4-MET solutions with concentrations of 0.1, 1 and 10wt% and could demonstrate that a 10wt% 10-MDP solution is effective to improve the adhesive performance of resin to titanium, especially when it was applied to pre-treat Ti prior to the application of Panavia Fluoro Cement. The molecular

weight of both 10-MDP and 4-MET is exactly 322.3. Thus, the respective solutions of each functional monomer have almost the same concentration in molarity.

In order to investigate the effect of 4-MET- and 10-MDP-based primers on resin bonding to titanium, we used two resin-based cements, Panavia Fluoro Cement and SuperBond C&B, which include 10-MDP and 4-MET as functional monomers, respectively. For SuperBond C&B, two techniques, the bulk-mix and the brush-dip technique were used following the manufacturer's instructions. The tensile bond strength of SuperBond C&B bonded to Ti was significantly higher when the bulk-mix technique was used than when SuperBond C&B was bonded using the brush-dip technique. In addition, failure analysis revealed that all specimens of SuperBond C&B applied following the brush-dip technique showed a mixed failure pattern, while all specimens failed cohesively when SuperBond C&B was bonded using the bulk-mix technique. Thus, in the remaining part of the study SuperBond C&B was applied following the bulk-mix technique.

Although no significant difference in tensile bond strength was determined to untreated Ti as to Ti treated with either 10-MDP or 4-MET in concentrations of 0.1, 1 and 10wt%, pre-treatment of Ti with any 10-MDP-based primer resulted in a higher tensile bond strength than when Ti was pre-treated with 4-MET in any of the three concentrations. Our results are in line with those of Taira *et al.*, who demonstrated that suitable durable bonding to Ti could be obtained when a methacrylate-phosphate primer in combination with a composite luting agent was used^{18,19}. We also have reported on the use of phosphoric acid to pre-treat Ti²⁰. Using X-ray photoelectron spectroscopy, we could demonstrate that P originating from phosphoric acid could clearly be detected on the surface of Ti, even when it was rinsed with distilled water. P was below the detection limit on the surface of untreated Ti. Maekawa *et al.* recently investigated the intensity of polyphosphoric acid adsorption on Ti and demonstrated that immersion of Ti into different concentrations of polyphosphoric acid increased the P/Ti ratio on the Ti surface in a polyphosphoric acid dose-dependent manner (unpublished data). Abe *et al.* reported that phospho-amino acids chemically and stably bonded to the Ti surface²¹. All the abovementioned data clearly suggest that phosphoric acid and its derivatives can be strongly adsorbed onto the Ti surface.

10-MDP is an acidic monomer included in other dental adhesive materials, such as self-etch adhesives (Fig. 1). Recently, it was reported that 10-MDP has a great potential to adhere to apatitic substrates such as the inorganic component of human hard tissues like enamel, dentin and bone^{22,23}. 10-MDP is an ester originating from the reaction of a bivalent alco-

hol with methacrylic acid and phosphoric-acid derivatives. XPS also revealed that P was detected when Ti was pre-treated with a 10-MDP solution, even after the surface was ultrasonically rinsed twice in an ethanol solution for 20 min. This result indicated that through its phosphate group the functional monomer 10-MDP strongly adsorbed onto Ti; It remained adsorbed despite thorough ultrasonic rinsing.

Pre-treatment of Ti with a 10-MDP-based primer is effective to improve the adhesive performance of Panavia Fluoro Cement to Ti. This must be attributed to the enhanced chemical interaction between resin and Ti. All specimens of Panavia Fluoro Cement failed mixed adhesive-cohesively, including areas where the resin-titanium interface failed adhesively. Thus, primers directly influenced the bonding effectiveness of Panavia Fluoro Cement to Ti. On the contrary, no significant difference in tensile bond strength of SuperBond C&B was determined for the untreated and six treated Ti surfaces. This may be the reason why failures occurred cohesively in the SuperBond C&B luting cement using the bulk-mix technique.

CONCLUSION

In conclusion, pre-treating Ti with a 10-MDP-based primer is effective to improve the adhesive performance of resin to titanium, especially when Panavia Fluoro Cement was used.

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