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Bonding of Dual-cured Resin Cement to Zirconia Ceramic
Using Phosphate Acid Ester Monomer and Zirconate Coupler

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Short title: Zirconia ceramic primer using phosphate acid ester monomer and
zirconate coupler

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Abstract: This study evaluated the shear bond strength of a dual-cured resin luting cement to pure zirconium (99.9%) and industrially manufactured yttrium-oxide-partially-stabilized zirconia ceramic, and the effect of MDP (10-methacryloyloxydecyl dihydrogen phosphate) primer (MP) and zirconate coupler (ZC) on bond strength. Two different-shaped pure zirconium and zirconia ceramic specimens were untreated or treated with various primers including different concentrations of MP containing phosphoric acid ester monomer (MDP) in ethanol, ZC containing a zirconate coupling agent in ethanol, or a mixture of MP and ZC. The specimens were then cemented together with dual-cured resin luting cement (Clapearl DC). Half of the specimens were stored in water at 37°C for 24 h and the other half were thermocycled 10,000 times before shear bond strength testing. The bond strengths of resin luting cement to both the zirconium and zirconia ceramic were enhanced by the application of most MPs, ZCs, and the mixtures of MP and ZC. No significant difference in shear bond strength for the group (MP2.0+ZC1.0) containing 2.0 wt% MP and 1.0 wt% ZC was observed between before and after thermal cycling for both zirconium and zirconia ceramic ($p > 0.05$). For the other primers, statistically significant differences in shear bond strength before and after thermal cycling were observed ($p < 0.05$). The application of the mixture of MP and ZC (MP2.0+ZC1.0) was effective for bonding between zirconia ceramic and dual-cured resin luting cement. This primer may be clinically useful as an adhesive primer for zirconia ceramic restoration.

INTRODUCTION

Increased patient demand for aesthetic and metal-free restorations has resulted in the proliferation of all-ceramic restorations.^{1,2} All-ceramic restorations can be created in many ways and using different materials, but computer-aided design and manufacturing (CAD/CAM) has become an increasingly interesting alternative to manual, casting, or pressing techniques. Clinical success of glass-infiltrated alumina ceramic³⁻⁵ and CAD/CAM-fabricated densely sintered high-purity alumina ceramic^{6,7} relies on high flexural strength and fracture resistance compared with other porcelains available.⁸⁻¹² Zirconia is a high flexural strength ceramic over 1,000 MPa¹³ that is about six times stronger than feldspathic porcelains, and it is used as an orthopedic material.¹⁴ Based on these improved physical properties compared to alumina-based ceramics, zirconia ceramic has recently been introduced in restorative dentistry. Polycrystalline zirconia is typically used in the tetragonal crystalline phase, partially stabilized with yttrium oxide (Y-TZP).¹⁵ Clinical applications of Y-TZP include use in all-ceramic cores and post systems^{16,17} and coping for complete coverage of all-ceramic crowns and fixed partial dentures.¹⁸⁻²⁰

Most ceramic restorations are adhesively luted to the prepared tooth, and various resin cements have been marketed.²¹ Hydrofluoric acid etching and silane coupling agents are not capable of providing as strong of a bond of resin cement to Y-TZP as conventional silica-based ceramics.²² Hydrolytically

stable bonds to Y-TZP ceramic have only been achieved after sandblasting the ceramic surface²³ and using commercially available resin cement containing a phosphate monomer.²⁴⁻²⁶ However, only limited information regarding the detailed effects of phosphate acid monomers on the zirconia surface has been reported.

Strong tensile bonding to pure base metals such as chromium and titanium and nickel-chromium and cobalt-chromium alloys has been achieved with a combination of adhesive primer containing 10-methacryloyloxydecyl dihydrogen phosphate (MDP) and composite resin cement.²⁷ Resin cement containing MDP bonds most strongly to cobalt-chromium alloy.²⁸ It is proposed that MDP monomers may be equally effective for strongly bonding between resin cement and zirconium as it is with other base metals. Zirconate coupling agent improved the bond strength between pure zirconium and resin luting cement.²⁹ The hypothesis that MDP monomer and/or zirconate coupler increases the bond between zirconia ceramic and resin luting cement has been proposed. Therefore, we examined and measured the shear bond strength of dual-cured resin luting cement to pure zirconium and Y-TZP ceramic treated with MDP primer and/or new zirconate coupler for clinical use as a primer for zirconia ceramic restoration.

MATERIALS AND METHODS

Pure zirconium and zirconia ceramic

Two different-shaped zirconium disks (10 mm and 6 mm in diameter x 2.0 mm thick) were manufactured from pure metal zirconium (99.9%, Furuuchi Chemical Co., Ltd, Tokyo, Japan) with a low-speed cutting saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA). The metal surface was sanded to a flat surface by hand-grinding on wet 320-, 400-, 600-, and 800-grid silicon carbide paper and cleaned ultrasonically in distilled water for 5 min, and this surface of zirconium served as the control (Cont.).

Industrially manufactured yttrium-oxide-partially-stabilized zirconia ceramic disks (95.3 wt% ZrO_2 stabilized by 4.7 wt% Y_2O_3 , Shinagawa Fine Ceramics Co., Ltd., Tokyo, Japan) with a diameter of 10 mm and 6 mm and a thickness of 2.0 mm were used for this study. The ceramic surface was polished to Ra 0.5 by the manufacture, and this surface served as the control (Cont.).

Primers and resin luting cement

Two primers of MDP primer (MP) and zirconate coupler (ZC) for pure zirconium and zirconia ceramic and a dual-cured resin luting cement (Clap pearl DC) were used in this study. The MDP monomer (10-methacryloyloxydecyl dihydrogen phosphate) was contained at 0.1, 0.2, 0.5, 1.0, and 5.0 wt% in the MP of ethanol solution, and the zirconate coupling agent

(2,2-di(allyloxymethyl)butyl trimethacryloyl zirconate) was contained at 0.25, 0.5, 1.0, and 2.0 wt% in the ZC of ethanol solution. The structural formulae of the MDP monomer and the zirconate coupling agent are shown in Figure 1. Several mixture primers of MP and ZC were also prepared. Other primer (Porcelain Bond Activator) was also used for zirconia ceramic. These descriptions are given in Table I.

Preparation of specimens

A piece of polyethylene tape with a circular hole 4 mm in diameter was positioned on the surface of the 10 mm diameter x 2.0 mm thick zirconium or zirconia ceramic specimen to control the area of the bond. On two sizes of zirconium or zirconia ceramic specimen surfaces, the prepared primers were applied for 10 s, air-dried for 5 s, and were then bonded together with a resin luting cement. For the controls, no prepared primers were applied. A sample holder secured the bonded specimens in a rigid position during bonding and controlled the cement film thickness to approximately 50 μm . Excess cement was removed before complete hardening of the resin luting cement. The dual-cured resin luting cement was irradiated from four directions for 40 sec, for a total exposure time of 160 sec using a visible-light-curing source (Quick Light, J. Morita Corp., Osaka, Japan) at a light intensity $> 400 \text{ mW/cm}^2$. The specimens were allowed to stand for 30 min at room temperature. The specimens were assigned randomly to one of 13 test groups for zirconium and

zirconia ceramics, and divided into two subgroups of seven specimens each. One of the two subgroups was stored in distilled water at 37°C for 24 h. The remaining subgroup was stored in distilled water at 37°C for 24 h and followed by 10,000 thermocycles between water baths (Rika-Kogyo, Hachioji, Japan) held at 4°C and 60°C with a dwell time of 1 min in each bath. Thermal cycling was performed to evaluate the durability of the bond.

Shear testing procedure

Shear tests were performed, using a method previously described²⁸, with a universal testing machine (DCS-500, Shimadzu Corp., Kyoto, Japan) at a crosshead speed of 0.5 mm/min.

The means of each group were analyzed by two-way ANOVA with the shear bond strength as the dependent variable and the types of primers and storage conditions of specimens as independent factors, and the Student-Newman-Keulas test with $p < 0.05$ was used to establish significance. Debonded zirconium or zirconia surfaces were observed under an optical microscope (SMZ-10, Nikon, Corp., Tokyo, Japan) to assess the location and type of bond failure. Failure modes were categorized as follows: A, adhesive failure at the zirconium or zirconia ceramic-resin luting cement interface; B, complex adhesive failure and cohesive failure within the resin luting cement.

RESULTS

Table II shows the shear bond strengths of the resin luting cement to the pure zirconium treated with one of 13 different surface treatments at 0 and 10,000 thermocycles. Regardless of the concentration of MP, the groups treated with MP showed significantly higher shear bond strength than those not treated ($p < 0.05$). The control group had zero bond strength after 10,000 thermocycles. The bond strength of groups in all concentrations of MP after thermal cycling decreased significantly compared with those before thermal cycling ($p < 0.05$). Surface treatment with ZC0.5 and ZC1.0 showed significantly greater shear bond strength compared with controls before thermal cycling ($p < 0.05$). However, after 10,000 thermocycles, all three ZC groups showed significantly lower bond strength than before thermal cycling ($p < 0.05$). The groups consisting of mixtures of MP and ZC showed similar shear bond strength before thermal cycling ranging from 49.2-57.6 MPa. Only for the MP1.0/ZC1.0 and MP2.0/ZC1.0 mixtures, there were no significant differences in the shear bond strengths before and after thermal cycling ($p > 0.05$).

Table III shows the shear bond strengths of resin luting cement to zirconia ceramic treated with one of 13 different surface treatments at 0 and 10,000 thermocycles. Silane coupling agent (PBA) was not effective for increasing shear bond strength before thermal cycling compared with control. The MP, ZC, and mixture of MP and ZC groups showed similar results as pure zirconium.

There were significant differences between bond strength before and after thermal cycling for all MP and ZC groups and four of the five groups of mixtures of MP and ZC ($p < 0.05$). Only the MP2.0+ZC1.0 group maintained its shear bond strength after 10,000 thermocycles among all the treatment groups.

Surface observation of the debonded specimens revealed that most specimens of the control and ZC groups for zirconium and zirconia ceramic showed interface failure between metal and resin luting cement and between ceramic and resin luting cement (Table IV). Most specimens of the MP groups for zirconium and zirconia ceramic showed complex adhesive failure and cohesive failure within the resin luting cement at thermocycle 0, and then adhesive failure at 10,000 thermocycles. Failure mode B was observed for most specimens of the MP2.0+ZC1.0 group regardless of thermal cycling.

DISCUSSION

The bond between silica-based ceramics to resin luting cements is well-established because etching with hydrofluoric acid and application of a silane coupling agent provides good bonding. A silane coupler has the property of increasing the wettability of the ceramic surface for the resin luting cement, thus improving the ability of the ceramic surface to adhere to resin cements. In addition, this facilitates the bonding between the silica based in

the ceramics and the matrix resin monomer in the luting cements.³⁰⁻³²

However, neither etching with hydrofluoric acid nor a silane coupling agent can reliably improve bond strength between zirconia ceramics with no silica content and resin cements because of the high resistance of acids.³³ There are only a few studies on the bonding methods of zirconia ceramics to resin luting cements.²⁴⁻²⁶ However, no information regarding the suggested reaction of the phosphate acid ester monomer contained in a commercial luting material or zirconate coupler with zirconia ceramic surface has been reported. Therefore, strong adhesion between the resin luting cement and zirconia is an important factor for successful zirconia-based ceramic restorations.

The MDP monomer may be as effective for creating a strong bond between resin cement and zirconium as other base pure metals and alloys^{27,28} because the surface of zirconium is coated with a passive film of zirconium oxide. In other words, it may be useful for zirconia because hydroxyl groups may be present on the zirconia surface. Silane coupling agent is effective for bonding between silica-based ceramic and resin cement. Zirconate coupling agents may enhance the bond between zirconia ceramic and resin luting cement as in the silane coupling agent. Therefore, as a first step, we evaluated the shear bond strength of a dual-cured resin luting cement to pure zirconium with experimental phosphoric acid ester monomer (MDP) and a new zirconate coupler. Then, the effectiveness of several primers for Y-TZP ceramic material was investigated for use as a clinical primer for zirconia ceramic restoration.

When pure zirconium and zirconia ceramic were primed with MP containing MDP, the shear bond strength of the resin luting cement before thermal cycling markedly improved compared with the control group. The phosphate ester monomer of the MDP was reported to bond directly to metal oxides such as chromium, nickel, aluminum, tin, titanium, and zirconium oxides.³⁴ The findings of the present studies suggest that the MDP monomer may bond chemically to the zirconium oxide layer coated on the zirconium surface. This is consistent with previous studies²⁴⁻²⁶, which showed that resin luting cements containing MDP can bond strongly to sandblasted zirconia. Hydrogen bonds may be formed between hydroxyl groups in the MDP monomer and hydroxyl groups on the zirconia ceramic surface.³⁵ However, these chemical bonds did not maintain their strength after thermal cycling. Failure mode analysis revealed that most specimens of the MP groups containing 0.5 and 1.0 wt% MDP showed adhesive failure at the zirconium or zirconia ceramic-resin luting cement interface for both zirconium and zirconia ceramic materials.

When pure zirconium and zirconia ceramic were treated with ZC containing 0.5 and 1.0 wt% zirconate coupling agent, shear bond strength was improved compared with the control group before thermal cycling. However, shear bond strength after thermal cycling decreased significantly more than that before it ($p < 0.05$). A coupling effect of the zirconate coupler to the zirconium²⁹ or zirconia ceramic was expected as in the silane coupler, showing coupling to the

silica or dental porcelain. Zirconate coupling agents might slightly bond with hydroxyl groups on the surface of zirconium or zirconia ceramic. The group (MP2.0+ZC1.0) treated with the mixture of 2.0 wt% MDP and 1.0 wt% zirconate coupling agent showed significantly greater shear bond strength after thermal cycling, and no significant decrease was observed between bond strength before and after thermal cycling ($p > 0.05$). Silane coupling agent is rapidly hydrolyzed in the presence of an acid monomer such as MDP. After that, the silane coupling agent can react with hydroxyl groups on the surface silica through the formation of siloxane bonds. Polysiloxane formation with a strong molecular structure is promoted by the acidity on the substrate surface treated with a silane coupling agent.³⁶ Therefore, stronger poly-molecular structural layers might be formed on the zirconia ceramic surface treated with the mixture primer (MP2.0+ZC1.0) of the zirconate coupling agent and the acid MDP monomer compared with single MP or ZC treatment. Hydrogen bonds between the MDP monomer or the zirconate coupling agent and adsorbed -OH on the zirconia surface might present as in Figure 2.

The bond to the ceramic substrates seems to depend on the presence of silica on the surface, which would be compatible with the silane coupling agents.³⁷ Thus, the silane coupler (PBA) did not promote bonding between the zirconia ceramic and resin luting cement in this study. The findings of the present study suggest that a primer mixture of an acid MDP monomer and a zirconate coupling agent is effective for strong bonding between resin luting cement and

zirconia ceramic. The Clapearl DC material does not contain an acid functional monomer such as MDP in contrast to other commercially available resin luting cements. Thus, adhesive acid functional monomers may not be necessary in resin luting cement for zirconia ceramic restorations if a primer containing this substance is used.

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