Effect of a silane and phosphate functional monomer on shear bond strength of a resin-based luting agent to lithium disilicate ceramic and quartz materials

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Abstract: This study examined the effect of silane and phosphate functional monomer on bond strengths between a resin-based luting agent joined to a lithium disilicate ceramic (IPS e.max) and silica (quartz) materials. The e.max and quartz specimens were assigned to 6 groups with different priming/bonding agents, namely, Clearfil Porcelain Bond Activator, Clearfil Photo Bond, Clearfil Photo Bond Universal with Clearfil Porcelain Bond Activator, Clearfil Photo Bond Catalyst with Clearfil Porcelain Bond Activator, Clearfil Photo Bond with Clearfil Porcelain Bond Activator, and unprimed. The corresponding specimens were bonded by using a resin-based luting agent (Panavia V5). Shear bond strengths were determined before and after 5,000 thermocycles. For both the e.max and quartz specimens, the Clearfil Photo Bond Universal with Clearfil Porcelain Bond Activator group had the highest pre- and post-thermocycling bond strength values. Combined use of silane in the acidic environment of a phosphate functional monomer and initiators enhances bond strength of a resin-based luting agent to e.max ceramic and quartz materials.

Keywords: bond strength; phosphate functional monomer; silane; silica-based ceramics.

Introduction

Because of their excellent aesthetic properties, high biocompatibility, and wear resistance, ceramic restorations are widely used for laminate veneers and fixed dental prostheses. Fracture resistance and long-term viability are better for high-strength ceramics (i.e., zirconium dioxide ceramics) than for silica-based ceramics (i.e., feldspathic porcelain, lithium disilicate ceramics) (1,2). However, silica-based ceramics have greater translucency and are less opaque than high-strength ceramics and are thus more likely to yield excellent aesthetic outcomes (3).

A strong, durable resin bond between the ceramic material and abutment teeth is required for the clinical success of ceramic restorations (4-6). In particular, the adhesive bond between silica-based ceramic restorations and abutment teeth must contend with the brittleness and imperfect mechanical properties of such restorations. Achieving a strong resin bond requires satisfactory micromechanical interlocking and chemical bonding to the ceramic surface (7-9). Hydrofluoric acid etching (7,9) and airborne-particle abrasion with aluminum oxide particles are the preferred intaglio surface treatments for achieving micromechanical interlocking (10,11). Subsequent silanization with a bifunctional silane forms a chemical interaction between the resin-based luting agent and silica-based ceramic, which is an important factor in ensuring an adequate bond to ceramics (12,13). Lithium disilicate ceramics were developed for use
with lost-wax and heat-pressed technique and with computer-aided design/computer-aided manufacturing (CAD/CAM) technology. These ceramics are widely used as an aesthetic restorative material because their flexural strength and fracture toughness are better than those of other silica-based ceramics (14).

Multicomponent ceramic bonding agents, which comprise a base monomer, adhesive functional monomer, solvent, and initiator, are frequently used for ceramic bonding (15,16). One-, two-, and three-bottle bonding agents are marketed by several manufacturers. Acid and/or heat are used during silane treatment, to enhance ceramic bonding (17,18). In addition, the acidic functional monomer in multicomponent ceramic bonding agents improves ceramic bonding because the accelerated condensation reaction is catalyzed by the acidic monomer (19). Although studies have investigated the bond strength of resin-based luting agents to lithium disilicate ceramics using a multicomponent ceramic bonding agent. In addition, this study determined the bond strength between a resin-based luting agent and silica material used an identical test protocol. The null hypotheses were that application of silane contained in a phosphate functional monomer would not enhance bond strength and that bond strength would not be affected by thermocycling.

**Materials and Methods**

The materials assessed in this study and their characteristics are summarized in Table 1. A total of 264 paired disk specimens (e.max specimens; 11.0 mm in diameter × 2.5 mm in thickness, or 8.0 mm in diameter × 2.5 mm in thickness) were fabricated from a lithium disilicate ceramic material (IPS e.max Press LT A2 shade, Ivoclar Vivadent, Schaan, Liechtenstein; Fig. 1A). In addition, 264 paired silica material disks (quartz specimens; 11.0 mm in diameter × 2.5 mm in thickness, or 8.0 mm in diameter × 2.5 mm in thickness) were prepared by cutting a 99.9% SiO₂ circular cylinder (Kokugo Co., Ltd., Tokyo, Japan; Fig. 1A). All disk specimens were prepared using an identical technique and were divided into six groups. The null hypotheses were that application of silane contained in a phosphate functional monomer would not enhance bond strength and that bond strength would not be affected by thermocycling.

### Table 1 Materials assessed in this study

<table>
<thead>
<tr>
<th>Material/Trade name</th>
<th>Code</th>
<th>Lot no.</th>
<th>Component</th>
<th>Manufacturer</th>
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</thead>
<tbody>
<tr>
<td>Lithium disilicate ceramic material</td>
<td></td>
<td></td>
<td>SiO₂: 57-80%, LiO₂: 11-19%, K₂O: 0-13%, P₂O₅: 0-11%, ZrO₂: 0-8%, ZnO: 0-8%, others: 0-10%</td>
<td>Ivoclar Vivadent, Schaan, Liechtenstein</td>
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<tr>
<td>Silica material</td>
<td></td>
<td></td>
<td>SiO₂: 99%</td>
<td>Kokugo Co., Ltd, Tokyo, Japan</td>
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<td>Quartz</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Priming/bonding agent</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Clearfil Photo Bond</td>
<td>CPB</td>
<td></td>
<td>MDP, HEMA, Bis-GMA, BPO, CQ, hydrophobic dimethacrylate</td>
<td>Kuraray Noritake Dental Inc., Tokyo, Japan</td>
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<td>Catalyst</td>
<td>CPBC</td>
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<td>Universal</td>
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<td>460025</td>
<td>Initiator, accelerator, ethanol</td>
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<tr>
<td>Clearfil Porcelain Bond Activator</td>
<td>Act</td>
<td>690031</td>
<td>3-TMSPMA, hydrophobic aromatic dimethacrylate, others</td>
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<td>Luting agent</td>
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<tr>
<td>Panavia V5</td>
<td>PV5</td>
<td>1G0046</td>
<td>Bis-GMA, TEGDMA, hydrophobic aromatic dimethacrylate, silanated barium glass filler, hydrophilic aliphatic dimethacrylate, fluorooaminosilicate glass filler, colloidal silica, accelerator, initiator</td>
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<td>A Paste</td>
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</tr>
<tr>
<td>B Paste</td>
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<td></td>
<td>Bis-GMA, hydrophobic aromatic dimethacrylate, hydrophilic aliphatic dimethacrylate, silanated barium glass, silanated aluminium oxide filler, colloidal silica, CQ, accelerator, pigments, others</td>
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</tr>
</tbody>
</table>

sequentially wet-polished with 400-, 800-, and 1,200-grit silicon carbide paper (Tri-M-ite Wetordry sheets, 3M, St. Paul, MN, USA). A piece of plastic tape (Star Traper-GP, Sakurai Co., Tokyo, Japan) with a hole (diameter, 5 mm) was placed on the surface of specimens (diameter, 11.0 mm), to standardize the bonding area (Fig. 1B).

The disk specimens were assigned to six groups of 11 specimens each, depending on the priming/bonding agent used for surface treatment, as follows: Clearfil Porcelain Bond Activator (Act; Kuraray Noritake Dental Inc., Tokyo, Japan), Clearfil Photo Bond (CPB; Kuraray Noritake Dental Inc.), Clearfil Photo Bond Universal (CPBU) with Clearfil Porcelain Bond Activator (CPBU+Act; Kuraray Noritake Dental Inc.), Clearfil Photo Bond Catalyst (CPBC) with Clearfil Porcelain Bond Activator (CPBC+Act; Kuraray Noritake Dental Inc.), Clearfil Photo Bond with Clearfil Porcelain Bond Activator (CPB+Act; Kuraray Noritake Dental Inc.), and unprimed specimens (UP). A microbrush (Micro Tip Applicator, GC Corp., Tokyo, Japan) was used to apply each priming/bonding agent as a bonding promoter to the surfaces of specimens with diameters of 11.0 mm and 8.0 mm (Fig. 1C). Then, the priming/bonding agent was allowed to gently air dry with oil-free air spray (Air Duster AD400FL, Orientec Inc., Misato, Japan).

The corresponding disk specimens were bonded by using a resin-based luting agent (Panavia V5, Kuraray Noritake Dental Inc.) in accordance with the manufacturer’s instruction (Fig. 1D). Disks with a diameter of 8.0 mm were bonded to disks with a diameter of 11.0 mm at a load of 5 N and were light-polymerized for 40 s with a light-polymerization device (Optilux 501, Kerr Corp., Middleton, WI, USA; Fig. 1E). After bonding, specimens were stored in a darkroom at 25°C for 30 min, after which they were immersed in distilled water at 37°C for 24 h (Fig. 1F). This point was defined as 0 thermocycles. Half the specimens (n = 11) were thermocycled with a thermal cycling device (Thermal Shock Tester TTS-1 LM, Thomas Kagaku Co. Ltd., Tokyo, Japan) for 5,000 thermocycles at 5°C and 55°C for 1 min dwell time (Fig. 1G).

Each specimen was mounted in a shear-testing jig (ISO TR 11405, Tokyo Giken Inc., Tokyo, Japan), and shear bond strength was measured with a universal testing machine (Type 5567, Instron, Canton, MA, USA) with a 5-kN load cell at a crosshead speed of 0.5 mm/min until failure (Fig. 1H).

Statistical analyses were performed with IBM SPSS Statistics, version 24.0, statistical software (IBM, Armonk, NY, USA). The results were primarily analyzed with the Kolmogorov-Smirnov test and the Levene test (IBM SPSS Statistics, version 24.0, IBM). At least one group did not exhibit a normal distribution on the Kolmogorov-Smirnov test. In addition, the Levene test did not show homoscedasticity. The Kruskal-Wallis test (IBM SPSS Statistics, version 24.0, IBM) was used to examine differences among test groups, after which the six groups were compared with the post-hoc Steel-Dwass test.
test for multiple comparisons (Kyplot 5.0, KyensLab, Tokyo, Japan). The Mann-Whitney U test was used to analyze differences in shear bond strengths, before and after thermocycling, for the same surface treatments. The level of statistical significance was set at 5%.

After shear bond testing, an optical microscope (Stemi DV4, Carl Zeiss MicroImaging GmbH., Göttingen, Germany) at ×32 magnification was used to examine the surfaces of debonded specimens to determine failure mode, which was categorized as follows: A, adhesive failure at the luting agent/ceramic interface; AC, combined adhesive and cohesive failure; and C, cohesive failure inside the ceramic material.

After shear bond testing, X-ray diffraction (XRD) was used to analyze the surfaces of representative specimens, including ground e.max and quartz specimens, resin-based luting agent, and e.max and quartz specimens. The specimens were positioned in the holder of the XRD device (MiniFlex II, Rigaku Corp., Tokyo, Japan). Data were collected at 30 kV and 15 A in a 2θ range from 3° to 90°.

**Results**

The results of shear bond testing and statistical analysis are shown in Table 2. For the e.max and quartz specimens, the Steel-Dwass test showed that the CPB+Act group had the highest shear bond strength of all groups, before and after thermocycling. The bond strength of the CPBC+Act group was significantly higher than that of the Act group, at 0 and 5,000 thermocycles, in both e.max and quartz specimens. Although the pre-thermocycling bond strength of the CPBU+Act and Act groups did not significantly differ in e.max (P = 0.898) or quartz (P = 0.478) specimens, post-thermocycling bond strength was significantly higher (P < 0.001) for the CPBU+Act group than for the Act group. All e.max and quartz specimens in the UP group had debonded after 5,000 thermocycles. The Mann-Whitney U test revealed that bond strengths in all groups were significantly lower after thermocycling.

The results of failure mode assessment are shown in Table 3. Among the quartz specimens, cohesive failure within the quartz material was frequent in the four silane treatment groups (Act, CPBC+Act, CPBU+Act, and CPB+Act). In addition, among e.max specimens, these four groups exhibited adhesive/cohesive failure. After thermocycling, adhesive/cohesive failure was predominant in CPB+Act group quartz specimens.

Figures 2 and 3 show XRD patterns of representative specimens. The peaks of SiO₂—(2θ = 38.0°, 42.8°, and 50.7°) and (2θ = 22.7°, 24.2°, and 25.6°)—were detected in the XRD patterns of the e.max ceramic material (Li₂Si₂O₅) (Fig. 2A) and resin-based luting agent (Fig. 2B), respectively. The XRD pattern of e.max specimens with combined adhesive/cohesive failure (Fig. 2C) corresponded to those of the e.max ceramic material (Fig. 2A) and resin-based luting agent (Fig. 2B). The representative XRD pattern for the quartz material shows the SiO₂ peak (2θ = 21.5°, 23.8°, and 26.7°) (Fig. 3A), as does the XRD pattern for the resin-based luting agent (Fig. 3B).

Figure 3C shows the XRD pattern for combined adhesive/cohesive failure in quartz specimens, and exhibits peaks corresponding to the quartz material (Fig. 3A) and luting agent (Fig. 3B).
Discussion

This study investigated the effect of a silane and phosphate functional monomer on shear bond strengths of a resin-based luting agent to silica-based ceramics after use of a multicomponent ceramic bonding agent. By using a combination of liquids, a three-liquid bonding agent was used to determine the effect of silane and phosphate functional monomers on the bond of a resin-based luting agent to silica-based ceramics. On the basis of the results obtained, the first null hypothesis—that application of silane contained in a phosphate functional monomer would not enhance bond strength—is rejected. The bond

<table>
<thead>
<tr>
<th>Group</th>
<th>e.max specimens</th>
<th>Quartz specimens</th>
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<tr>
<td></td>
<td>A</td>
<td>AC</td>
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<td>0 thermocycles</td>
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<tr>
<td>UP</td>
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<tr>
<td>Act</td>
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<td>3</td>
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5,000 thermocycles

<table>
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<tr>
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<th>e.max specimens</th>
<th>Quartz specimens</th>
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<tr>
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<tr>
<td>CPB+Act</td>
<td>9</td>
<td>2</td>
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A: adhesive failure at the resin-based luting agent/ceramic material interface, AC: combined adhesive/cohesive failure, C: cohesive failure within the ceramic material.

Fig. 2 XRD diffraction patterns of an (A) e.max ceramic material, (B) resin-based luting agent (PV5), and (C) e.max specimen exhibiting combined adhesive/cohesive failure after shear bond testing.

Fig. 3 XRD diffraction patterns of a (A) quartz material, (B) resin-based luting agent (PV5), and (C) quartz material specimen exhibiting combined adhesive/cohesive failure after shear bond testing.
strengths between a lithium disilicate ceramic material or quartz material and a resin-based luting agent were enhanced by the combination of silane and phosphate functional monomers. In addition, bond strength significantly decreased after thermocycling in all groups. Thus, the second null hypothesis—that bond strength would not be affected by thermocycling—is also rejected.

For e.max and quartz specimens, bond strengths before and after thermocycling were significantly higher in the CPB+Act group specimens, which contain phosphate functional monomer (10-methacryloyloxydecyl dihydrogen phosphate [MDP]), silane, and initiator. In addition, combined adhesive/cohesive failure was frequently observed in quartz specimens and in several e.max specimens in the CPB+Act group. This suggests that combined use of a silane (3-TMSPMA, 3-trimethoxysilylpropyl methacrylate) under the acidic environment of the MDP monomer and initiators contained in CPBU enhances the bond strength of a resin-based luting agent to e.max ceramic and quartz material. This result is supported by the finding that the pre- and post-thermocycling bond strengths of the CPBC+Act group were significantly higher than those of the Act group in e.max and quartz specimens. The strong bond likely resulted from activation of silane in the phosphate functional monomer (MDP), which is caused by a pH decrease in the priming/bonding agent (19,23-25). Chemical bonding of silane to silica, through a siloxane network, is accelerated by acidic functional monomers (11,12,26). Moreover, application of initiators contained in CPBU and a silane in the activator provided a durable bond between a lithium disilicate ceramic material or quartz material and a resin-based luting agent. The present results are consistent with those of previous studies (19,27,28).

The bond strength values in all groups of e.max and quartz specimens were significantly lower after thermocycling, which is commonly used as an artificial aging method in evaluating resin bonding to ceramic materials (29-31). Previous studies (32,33) showed that thermocycling causes hydrolytic degradation at bonding interfaces and thermal stress due to differences in the coefficient of thermal expansion between tested materials.

In this in vitro study, the quartz of a silica material was used to identify a satisfactory surface treatment for SiO2. Although no cohesive failure occurred within e.max specimens, cohesive failure of quartz material was seen in some groups treated with primer agents containing a silane, perhaps because of inferior fracture toughness values for the quartz material (34,35). Hence, future studies should comprehensively evaluate bonding performance between silica and resin-based luting agents.

Within the limitations of this study, it can be concluded that combined use of a silane (3-TMSPMA) under the acidic environment of a phosphate functional monomer (MDP) and initiators enhances bond strength of a resin-based luting agent to both e.max ceramic material and quartz material.

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Conflict of interest
The authors have no conflict of interest to declare.

References


