INTRODUCTION

As digital impression and in-office machining increase in prevalence, materials such as laboratory-processed resin composite have been developed to optimize single-visit crown delivery. Computer-aided design/computer-aided manufacturing (CAD/CAM) composite blocks polymerized in the laboratory can be converted into restorations more efficiently as they can be fabricated faster and eliminate the need for light polymerization and heat treatment after milling the restorations. The standardized polymerization of CAD/CAM composite blocks under high pressure and temperature yields significantly better mechanical properties and color stability. Although it is true that the reported flexural strength of a representative CAD/CAM composite blocks was just under half of that of more commonly utilized CAD/CAM ceramic materials, the former have shown a higher resistance to fatigue loading than the latter. In addition, CAD/CAM composite blocks show lower wear than the other ceramic materials, and are thought to be a suitable materials even for full coverage posterior restorations.

However, it can be difficult to achieve a strong bond between CAD/CAM composite blocks and resin luting cements due to the high degree of conversion of resin monomers in the CAD/CAM composite blocks. A reliable bond between the prepared tooth and the internal part of the restoration is important to the long-term success of the restorations. There are two different interfaces in the adhesive luting of restorations: (i) the interface between the tooth structure and the resin luting cements; and (ii) the interface between the resin luting cement and the surface of CAD/CAM composite blocks. The bond to tooth structure with resin luting cements has been extensively researched, whereas much less is known about the other interface, specifically the interface between the resin luting cements and the CAD/CAM composite blocks. Therefore, it is crucial to establish the treatment methods appropriate to each surface to yield optimal bonding outcomes, and to establish adequate and durable bonding for the restorations.

Durable bonding between different substrates takes place on the basis of chemical and mechanical adhesion properties. Various surface treatment techniques are used to mechanically roughen the surface to achieve better bond strength. It has been reported that the bond strength between CAD/CAM composite blocks and resin luting cements can be significantly improved by aluminum-particle abrasion and silanization. In addition to mechanical retention, a strong chemical bond is required to obtain long-term clinical results. A reliable chemical bond to ceramic-based materials can be obtained with silanization, and it is reasonable to assume that silane has the ability to bond to fillers in CAD/CAM composite blocks. In some commercial adhesive primers, a mixture of silane and phosphoric acid/ester primers is used to improve the bonding performance of resin luting cement. Some studies have determined that the use of a silane or adhesive primer or both can improve the bond to CAD/CAM composite blocks.

When considering the composition of CAD/CAM composite blocks, the exposure of filler particles on the surface is material dependent, because filler contents, particle sizes, shapes, and distributions are different in different types of CAD/CAM composite blocks. Therefore, it is probable that the effectiveness of silanization
is not sufficient in some materials. In order to obtain durable bonds to CAD/CAM composite blocks, different approaches are necessary involving surface modification of the resin matrix of CAD/CAM composite blocks. Methyl methacrylate (MMA) has high wetting properties due to its lower molecular weight, and it is assumed that a low molecular weight primer may improve surface properties and achieve durable bond to CAD/CAM composite blocks. However, limited information is available about the effectiveness of such treatment methods in improving the bonding performance of resin luting cements to CAD/CAM composite blocks.

In the present study, we evaluated the influence of the surface treatment of CAD/CAM composite blocks on the bonding performance of resin luting cements in terms of the bond strengths and surface free energies of CAD/CAM composite blocks. Specifically, we assessed differences in bond strength and surface-free energy with different surface treatments. The null hypotheses in this study are that differences in the surface treatment of CAD/CAM composite blocks do not affect (1) bonding performance of resin luting cements, or (2) the surface free energy.

**MATERIALS AND METHODS**

**Study materials**

The materials used in this study are listed in Table 1. The resin luting cement used were dual-cured resin luting cement Block HC Cem (Shofu, Kyoto, Japan), and 4-META/MMA-TBB resin cement Super-Bond. The two CAD/CAM composite blocks evaluated were Cerasmart (GC, Tokyo, Japan) and VITA Enamic (VITA Zahnfabrik, Bad Säckingen, Germany). The silane coupling agent (Porcelain Primer, Shofu) and a primer (HC Primer, Shofu) were used.

**Specimen preparation**

CAD/CAM composite blocks were obtained perpendicularly to the longitudinal axis of the blocks using a low-speed saw (Isomet 1000, Buehler, Lake Bluff, IL, USA) to cut the block into four 2-mm-thick sections. Each sectioned CAD/CAM composite blocks was then mounted in self-curing acrylic resin (Tray Resin II, Shofu) and placed under water to limit the temperature rise caused by the exothermic polymerization of the acrylic resin. The cementation surfaces of CAD/CAM composite blocks were ground flat for surface standardization.

| Table 1 | Materials in this study used and their main components |
|---|---|---|---|---|
| **Resin cement** | **Main component** | **Manufacturer** | **Lot No.** |
| Block HC Cem | A: UDMA, fluoroalumino silicate glass, glass powder, initiator, others | Shofu, Kyoto, Japan | 011601 |
| | B: UDMA, 2-HEMA, carboxylic acid monomer, zirconium silicate, initiator, others | | |
| Super-Bond C&B | Poly (MMA) | Sun Medical, Moriyama, Japan | RG1 |
| Super-Bond L-Type Clear | | | |
| Super-Bond Quick Monomer | MMA, 4-META | Sun Medical | MV2 |
| Super-Bond Catalyst V | TBB, TBB-O, hydrocarbon | Sun Medical | MT21F |
| **CAD/CAM composite block** | **Main component** | **Manufacturer** | **Lot No.** |
| Cerasmart | Bis-MEPP, UDMA, DMA, silica, barium glass | GC, Tokyo, Japan | 1702211 |
| VITA Enamic | UDMA, TEGDMA, feldspar ceramic enriched with aluminum oxide | VITA Zahnfabrik Bad Säckingen, Germany | 65360 |

<table>
<thead>
<tr>
<th><strong>Silane coupling agent/ Primer</strong></th>
<th><strong>Main component</strong></th>
<th><strong>Manufacturer</strong></th>
<th><strong>Lot No.</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Porcelain Primer</td>
<td>anhydrous ethanol, silane coupling agent, anhydrous maleic acid, others</td>
<td>Shofu</td>
<td>071528</td>
</tr>
<tr>
<td>PZ Primer</td>
<td>A: MMA, phosphoric acid monomer, others</td>
<td>Sun Medical</td>
<td>A: RG1</td>
</tr>
<tr>
<td></td>
<td>B: MMA, silane coupling agent</td>
<td></td>
<td>B: RF1</td>
</tr>
<tr>
<td>HC Primer</td>
<td>UDMA, MMA, acetone, initiator, others</td>
<td>Shofu</td>
<td>031603</td>
</tr>
<tr>
<td>Super-Bond activated liquid</td>
<td>Quick monomer liquid mixed with Catalyst V</td>
<td>Sun Medical</td>
<td>—</td>
</tr>
</tbody>
</table>

UDMA: urethane dimethacrylate, HEMA: 2-hydroxyethyl methacrylate, MMA: methyl methacrylate, 4-META: 4-methacryloyloxyethyl trimellitate anhydride, TBB: tri-n-butyl borane, Bis-MEPP: 2,2-bis[4-(2methacryloyloxyethoxyphenyl)] propane, DMA: dimethacrylate, TEGDMA: triethyleneglycol dimethacrylate.
with P120 and P400 silicon-carbide papers (Struers, Cleveland, OH, USA) under continuous water cooling using a grinder/polisher (EcoMet 4, Buehler). These surfaces were then washed with an air-water spray and air dried using a dental three-way syringe 5 cm above the surface and with an air pressure of 0.3 MPa. Then, the surfaces were aluminum particle abraded with 50-µm Al₂O₃ particles for 10 s with an air pressure of 0.3 MPa, and then air dried with three-way syringe.

Shear bond strength (SBS) testing

A flow chart of the pretreatment of CAD/CAM composite blocks surface is presented in Fig 1. All sections were randomly divided into three groups according to surface treatment: 1) silane coupling agent application (SC) group, 2) primer application (PR) group, and 3) SC+PR group. After surface treatment, resin luting cement was condensed into a metal mold (2.38 mm in diameter, 3.0 mm in height) on the treated CAD/CAM composite block surface. Then, the placed cement was light polymerized for 30 s parallel to the cement interface with a quartz-tungsten-halogen (QTH) curing unit (Optilux 501, Kerr, Orange, CA, USA). The light intensity (>800 mW/cm²) of the QTH curing unit was monitored using a curing radiometer (model 100, Kerr). After 10 min, the specimens were stored in a dark room in 37°C distilled water for 24 h.

After the storage periods, specimens were loaded to failure at 1.0 mm per min with a universal testing machine (Type 5500R, Instron, Canton, MA, USA). The bond strength values were calculated from the peak load at failure divided by the bonded surface area. After testing, the bonding sites of metal mold and CAD/CAM composite blocks were observed under an optical microscope (SZH-131, Olympus, Tokyo, Japan) at a magnification of ×20 to determine the bond failure mode. Based on the percentage of substrate area (resin luting cement–CAD/CAM composite blocks), the types of bond failure were recorded as adhesive, mixed, cohesive failure in resin cement, and cohesive failure in CAD/CAM composite block.

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**Fig. 1** Experimental protocol in this study.
Surface free energy (SFE) measurements

The specimens for measurement of SFE were prepared in the same way as described in the bond strength test section. Contact angles of specimens were measured to analyze the surface characteristics of each treated CAD/CAM composite block surface. The SFE was determined by measuring the contact angles on the surface of the three test liquids, 1-bromonaphthalene, diiodomethane, and distilled water, each had known SFE parameters\(^\text{14}\). A contact angle meter (Drop Master DM 500, Kyowa Interface Science, Saitama, Japan) was connected to a charge-coupled device camera to allow automatic measurement of the contact angles.

For each test liquid, the equilibrium contact angle (\(\theta\)) was measured in ten enamel specimens for each condition. Sessile drops of each liquid measuring 1.0 \(\mu\text{L}\) in volume were dispensed at 23±1°C using a micro-pipette. The SFE parameters of the solids were then calculated based on the fundamental concepts of wetting. The Young-Dupré equation describes the adhesion between a solid (S) and liquid (L) that are in contact (\(W_{SL}\)), the interfacial free energy between the solid and the liquid (\(\gamma_{SL}\)), and the SFE of the liquid and solid (\(\gamma_s\) and \(\gamma_b\), respectively), as follows:

\[
W_{SL}=\gamma_s+\gamma_b-\gamma_{SL}=(1+\cos\theta)\frac{\gamma_s}{h}.
\]

The Fowkes equation can be extended using the Kitazaki-Hata approach\(^\text{15}\), as follows:

\[
\gamma_{SL} = \gamma_s^L + \gamma_b^S - 2\left(\gamma_s^L \gamma_b^S + \gamma_s^b \gamma_b^L - 2\gamma_s^L \gamma_b^s\right)^{1/2},
\]

where \(\gamma_s\), \(\gamma_b\), and \(\gamma^s\), \(\gamma^b\) are dispersion force, polar (permanent and induced) force, and hydrogen-bonding force, respectively, and they are components of the SFE (\(\gamma\)). \(\theta\) values were determined for all three test liquids, and the surface-energy parameters of treated surfaces were calculated according to the equations using add-on software and the interface measurement and analysis system (FAMAS; Kyowa Interface Science). A statistical power analysis indicated that at least eight samples were necessary for effective measurement of SFE. Therefore, this experiment was initially performed with sample sizes of ten. After gathering the data, post hoc power tests were performed, and these tests indicated that the sample size was adequate.

Statistical analysis

Before analysis of variance (ANOVA), homogeneity of variance (Bartlett’s test) and normal distribution (Kolmogorov-Smirnov test) were confirmed for the data for each group. One-way ANOVA followed by Tukey’s honestly significant difference (HSD) test (\(\alpha=0.05\)) was used for analysis of the bond strength and SFE data. The statistical analysis was done with statistical analysis software system (Sigma Plot, ver. 11.0, SPSS, Chicago, IL, USA).

Scanning electron microscopy (SEM) observation

Ultrastructural observations of resin cement/bock material interfaces were conducted after embedding bonded specimens in epoxy resin (Epon812, Nisshin EM, Tokyo, Japan), and incubating them at 37°C for an additional 12 h. Embedded specimens were sectioned, and surfaces of cut halves were polished using a grinder-polisher (Ecomet 4/Automat 2, Buehler) with #600, #1200, and then #4000 grid silicon carbide papers. Surfaces were finally polished on a special soft cloth using diamond paste down to 0.25 \(\mu\text{m}\) particle size (DP-Paste, Struers, Ballerup, Denmark). These surfaces were then subjected to argon-ion beam etching (Type EIS-200ER, Elionix, Tokyo, Japan) for 30 s with the ion beam (accelerating voltage, 1.0 kV; ion current density, 0.4 mAm\(^{-2}\)) directed perpendicular to the polished surface. Surfaces were finally coated in a vacuum evaporator (Quick Coater Type SC-701, Sanyu Electron, Tokyo, Japan) with a thin film of gold and were observed using a SEM instrument (ERA-8800FE, Elionix) at an accelerating voltage of 10 kV.

RESULTS

The mean SBS of Block HC Cem to CAD/CAM composite blocks with different surface treatments ranged from 3.2±2.1 to 17.6±1.5 MPa for Cerasmart, while the corresponding values for VITA Enamic ranged from 15.9±1.2 to 18.5±1.6 MPa (Table 2). For Cerasmart, Primer and Silane+Primer groups showed significantly higher SBS compared to Silane group. For Silane group,

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Cerasmart</th>
<th>VITA Enamic</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC group</td>
<td>3.2 (2.1)</td>
<td>18.5 (1.6)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>PR group</td>
<td>14.8 (2.5)</td>
<td>16.5 (2.1)</td>
<td>0.347 NS</td>
</tr>
<tr>
<td>SC+PR group</td>
<td>17.6 (1.5)</td>
<td>15.9 (1.2)</td>
<td>0.347 NS</td>
</tr>
</tbody>
</table>

Unit: MPa, \(n=10\), values in parenthesis indicate standard deviations. Within CAD/CAM resin composite, means with the same lower-case letter are not significantly different (\(p>0.05\)). p-Value indicates the comparison between different CAD/CAM composite block. NS=no significant difference.

Fracture mode: [interface failure/cohesive failure in resin cement/cohesive failure in CAD/CAM composite block]
Table 3 Influence of surface treatment of CAD/CAM composite block on bond strength of Super-Bond

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Cerasmart</th>
<th>VITA Enamic</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC group</td>
<td>11.6 (0.9)&lt;sup&gt;a&lt;/sup&gt; [6/0/4]</td>
<td>11.3 (1.0)&lt;sup&gt;a&lt;/sup&gt; [6/0/4]</td>
<td>0.996 NS</td>
</tr>
<tr>
<td>PR group</td>
<td>14.1 (1.3)&lt;sup&gt;b&lt;/sup&gt; [8/0/2]</td>
<td>14.8 (2.0)&lt;sup&gt;b&lt;/sup&gt; [8/0/2]</td>
<td>0.854 NS</td>
</tr>
<tr>
<td>SC+PR group</td>
<td>15.6 (1.5)&lt;sup&gt;b&lt;/sup&gt; [4/0/6]</td>
<td>16.0 (1.1)&lt;sup&gt;b&lt;/sup&gt; [4/0/6]</td>
<td>0.985 NS</td>
</tr>
</tbody>
</table>

Unit: MPa, n=10, values in parenthesis indicate standard deviations. Within CAD/CAM composite block, means with the same lower-case letter are not significantly different (p>0.05). p-value indicates the comparison between different CAD/CAM composite block. NS=no significant difference. [Fracture mode]: [interface failure/cohesive failure in resin cement/cohesive failure in CAD/CAM composite block]

Fig. 2 Representative SEM images of the cement (Block HC Cem) bonded interfaces with different surface treatments. A: Cerasmart with silane coupling agent (×10,000), B: Enamic with silane coupling agent (×10,000), C: Cerasmart with primer (×10,000), D: Enamic with primer (×10,000), E: Cerasmart with silane coupling agent+primer (×10,000), F: Enamic with silane coupling agent+primer (×10,000). Arrows indicate gaps between cement and CAD/CAM composite block.
surface treatments on SBS, higher values were obtained for Silane+Primer groups for both composite blocks. For both composite blocks, the predominant mode of failure for debonded specimens was adhesive failure for Primer groups, while cohesive failure in composite blocks increased in Silane and Silane+Primer groups.

Representative SEM images of the cement bonded interfaces are shown in Figs. 2 and 3. For the Block HC Cem, tight interfaces of the resin cements to CAD/CAM composite blocks were observed except for Cerasmart with the Silane group (Fig. 2). In particular, Silane group of Cerasmart, several gaps could be observed along the cement-block interfaces (arrows in Fig. 2). Further, the cement could not infiltrate into the cracks that had propagated sub-surface along the filler particles (arrows in Fig. 2). For the Primer and Silane+Primer groups, the primer layers of their thickness around 1–3 μm could be identified on roughened sandblasted surface of the composite blocks. For the Super-Bond, tight interfaces of the resin cements to CAD/CAM composite blocks were observed for Cerasmart and Enamic with the Silane+Primer group (Fig. 3). For Silane group and Primer group Cerasmart and Enamic, several gaps could be observed along the cement-block interfaces (arrows in Fig. 3).

The SFE and their components resulting from the different surface treatments are shown in Figs. 4 and 5. Dispersion force \( \gamma_s^{\text{d}} \) showed a similar SFE of approximately 40 (mN·m\(^{-1}\)) for all the tested groups. For the Block HC Cem, the total free energy \( \gamma_s \) of the initial group in baseline for Cerasmart was 51.3 (mN·m\(^{-1}\)), and for Enamic was 58.4 (mN·m\(^{-1}\)). For both composite blocks, the silane group showed significantly higher \( \gamma_s \) values than the other groups. In particular, the polar force \( \gamma_s^{\text{p}} \) and the hydrogen-bonding forces \( \gamma_s^{\text{h}} \) in the silane groups showed significantly higher values than the baseline groups.

The \( \gamma_s \) value in Super-Bond ranged from 51.3 to 70.6 (mN·m\(^{-1}\)) for Cerasmart, and 54.2 to 69.9 (mN·m\(^{-1}\)) for Enamic. When the primer was applied to both resin blocks, significantly higher \( \gamma_s \) values (from 68.8 to 70.6 mN·m\(^{-1}\)) obtained for both resin blocks comparing to

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**Fig. 3** Representative SEM images of the cement (Super-Bond) bonded interfaces with different surface treatments.
A: Cerasmart with silane coupling agent (×10,000), B: Enamic with silane coupling agent (×10,000), C: Cerasmart with primer (×10,000), D: Enamic with primer (×10,000), E: Cerasmart with silane coupling agent+primer (×10,000), F: Enamic with silane coupling agent+primer (×10,000). Arrows indicate gaps between cement and CAD/CAM composite block.
those of baseline and silane groups (from 51.3 to 58.4 mN/m) due to higher $\gamma_b$ values (from 26.1 to 26.5 mN/m).

**DISCUSSION**

In the present study, the bonding performance of resin luting cements to CAD/CAM composite blocks was evaluated. The different surface treatments of CAD/CAM composite blocks affected the bonding performance of resin luting cements and the SFE. Therefore, the null hypotheses that surface treatments do not affect (1) the bonding performance of resin luting cements, or (2) the SFE were both rejected.

Cementation technique is important to ensure clinical success and longevity of a restoration. In order to establish a strong and durable bond, which is necessary for the biomechanical aspect of the restoration system, appropriate treatment of the respective bonding surfaces is crucial. Various surface treatments with mechanical and chemical methods have been investigated to improve the bonding of CAD/CAM composite block. Alteration of surface texture of CAD/CAM composite block for higher bonding performance can be created through physically airborne particle abrasion with alumina and chemically etching with hydrofluoric acid. Alumina airborne particle abrasion creates a rough pitted surface, whereas, hydrofluoric acid etching dissolves filler particles leaving behind a honeycomblike appearance. Some studies reported superior bond strength to CAD/CAM composite block following airborne particle abrasion, others reported the use of a silane or adhesive primer or both can improve the bond to CAD/CAM composite block.

In this study, the influence of chemically alterations of adherent surfaces of CAD/CAM composite block was investigated.

Theoretically, chemical bonding between methacrylate monomers is a possible bonding mechanism between resin cement and resin based restorative material. Methacrylate monomers from the resin cement
Fig. 5 The SFE of CAD/CAM composite blocks (Cerasmart and Enamic) in different surface treatments (Super Bond group).

may copolymerize with unreacted C=C double bonds of the polymeric material when there exist\textsuperscript{46}. However, if there is a high degree of conversion of C=C double bonds in the resin material, bonding can mainly be attributed to mechanical roughening of the adherent surface or chemical alternation of the materials. The results of the present study showed that the effect of silane and primer treatments were resin cement and CAD/CAM composite block dependent. The bonding mechanism of Block HC Cem using HC Primer, which contains UDMA, MMA, acetone and others, was considered the scenario described below. Methacrylate polymers can be caused to swell by applying acetone, and MMA to establish an interpenetrating network with CAD/CAM composite blocks. Wetting the polymeric resin surface with adhesive resin or monomer liquid leads to swelling of the polymer network, which is reported to enhance adhesive bonding\textsuperscript{19}. And also, acetone was regarded as appropriate solvent to swell the polymer surface and in turn to increase its permeability for the penetration of the UDMA/MMA mixture as a prerequisite to build up an interpenetrating network.

A conventional 4-META/MMA-TBB resin cement (Super-Bond C&B) is composed of a liquid, including a functional monomer (4-META) in MMA with a chemical-cure initiator (TBB) and a polymethyl methacrylate (PMMA) powder. The molecular weight of MMA (\textit{mw}=100) is the smallest among the dental polymerizable methacrylates, leading to more easily penetration into the CAD/CAM composite blocks. It is generally accepted that, for MMA/PMMA denture base materials, grinding the surface of the denture tooth and wetting it with monomer is a pre-requisite to obtain clinically reliable bond strength\textsuperscript{20}. So the bonding mechanism of resin cement to CAD/CAM composite block is thought to be based on an interpenetrating network or a covalent bond\textsuperscript{21}.

From SEM images of the cement bonded interfaces of the Block HC Cem, several gaps could be observed along the cement-block interfaces Silane group of Cerasmart.
Further, the cement could not infiltrate into the cracks that had propagated sub-surface along the filler particles (arrows in Fig. 2). For the Primer and Silane+Primer groups, the primer layers of their thickness around 1–3 μm could be identified on roughened sandblasted surface of the blocks. For the Super-Bond, tight interfaces of the resin cements to CAD/CAM composite blocks were observed for CeramSmart and Enamic with the Silane+Primer group (Fig. 3). For Silane group and Primer group of CeramSmart and Enamic, several gaps could be observed along the cement-block interfaces (arrows in Fig. 3).

Measurement of contact angles with different liquid droplets is a common method to determine the SFE of a material. In the present study, three different liquids with different γL were used for the calculation of the SFE of the CAD/CAM composite block surfaces. Diiodomethane shows lower surface tension and higher viscosity than water. Therefore, it is important to understand the components of the CAD/CAM composite block surface. A crown with a CAD/CAM composite block was treated with primers and silane to improve SFE, it did not improve the SBS of HC Block .

CONCLUSION

Within the limitations of the present study, it may be concluded that not only silane application but also primer application might be more effective in increasing bonding performance of resin cements to the CAD/CAM composite block. Future studies should examine the effect of pretreatment with the combination of silane and primer on the bonding durability of resin luting cement to CAD/CAM composite blocks.

CONFLICT OF INTEREST

The authors of this manuscript certify that having no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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REFERENCES