Esthetic and bonding enhancements of tooth colored indirect restorations

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CHAPTER 4

The Effect of Adhesives with Various Degrees of Hydrophilicity on Resin-Ceramic Bond Durability.

4.1 Abstract

Objective. To investigate the role of different acid surface treatments and hydrophilic and hydrophobic bonding agents on resin-ceramic bond durability.

Materials and methods. Two resin cements, Tetric Flow and Nexus 2, were applied to CAD/CAM CEREC Vitarloc with six bonding strategies: 1: HF-etching and silanization, 2: HF-etching, silanization and application of a hydrophilic bonding agent, 3: HF-etching, silanization and application of a hydrophobic bonding agent, 4: H₃PO₄-treatment and silanization, 5: H₃PO₄-treatment, silanization and application of a hydrophilic bonding agent, and 6: H₃PO₄-treatment, silanization and application of a hydrophobic bonding agent. The hydrophilic agents were Syntac Single Component and OptiBond Solo Plus. The hydrophobic agent was Visio Bond. After 1 d water storage at 37°C, 1 mm² rectangular microbars were cut for the μTBS test (microtensile bond strength test). The microbars were subjected to a tensile load using a modified testing device immediately after trimming and after 7 d and 28 d water storage. The fractured specimens were examined with a stereomicroscope and SEM to determine the failure mode.

Results. HF-etching resulted in significantly higher μTBS than H₃PO₄ treatments (P<0.001). The 1 d μTBS with hydrophilic bonding agents was significantly higher than with the hydrophobic bonding agent (P<0.001), but decreased with time after water storage (P<0.001), while bonds with the hydrophobic bonding agent remained stable. The percentages of adhesive failures after 1 d, 7 d and 28 d were 60, 86 and 94, respectively.

Conclusion. Bonding agents which contain hydrophilic monomers have a negative influence on the resin-ceramic bond durability.
4.2 Introduction

Bonding of resin to ceramic materials plays an important role in dentistry particularly now, since the use of ceramics as indirect esthetic restorations has increased substantially.

During and immediately after polymerization of the resin composite the bond should be able to withstand the shrinkage stresses developed during setting.[1,2] It has been shown that these stresses may reach high values, due to the unfavorable C-factor for cement layers.[3] This occurs, when the surrounding tooth structure is rigid and not able to yield, like in class I, III and V indirect restorations.[3] In class II restorations where cusps can yield, the stresses are expected to be lower and less damaging for the bond. Because cement layers are thin, cusp displacement will only be small and not lead to post operative pain as frequently seen in direct resin composite restorations[4] with significant cusp movements.[5]

Also for the long term, conservation of the bond is essential. Various investigations have shown that adhesive resin cements increase the fracture resistance of indirect ceramic restorations.[6-8] Therefore, loss of adhesion will not only lead to leakage but also weaken the restoration.

The vulnerability of ceramic materials to fracture may also result in smaller or larger pieces chipping off from the restoration in particular intraorally, where the restoration is subjected to impact and cyclic (fatigue) loading. Removing and remaking of chipped ceramic restorations could be time consuming and costly with possibly sacrificing additional sound tooth structure. Using a resin composite, as a repairing material may be a better option.

Early approaches to ceramic repair and in general to bonding to ceramic surfaces, relied on macromechanical retention by means of grooves or undercuts.[9] Nowadays, bonding can be accomplished by both micromechanical and chemical alteration of the surfaces to be bonded to.

Hydrofluoric acid (HF) is commonly used to etch the bonding surface of indirect porcelain restorations.[10,11] To avoid working with the hazardous HF, acidulated phosphate fluoride[12], and phosphoric acid (H₃PO₄) were also investigated as alternatives.[13,14] However, their validity in achieving adequate bonding is still controversial.[15]

The use of silane as an organofunctional coupler, which is capable of forming chemical bonds between polymers and inorganic substances, is well known in the literature as a chemical method for bond enhancement.[13,16-19]

A significant factor to improve the adaptation of the repairing composite or resin cement to the surface of the indirect ceramic restoration, is the use of an intermediate bonding agent.[20] Most of the current bonding agents include hydrophilic monomers and solvents to promote adhesion to dentin. Many of these bonding agents are indicated by the manufacturer to be of
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multipurpose use, capable for bonding not only to enamel and dentin, but also to composites, metals and ceramics. However, little is known about the contribution of these hydrophilic dentin-bonding agents to the bond strength and their effect on bond durability.

Challenging the bond by water storage, thermal cycling and/or fatigue loading are the conditions most often used to test the durability of the resin-ceramic bond, but it is not clear for how long the samples should be stored in order to reveal the effect of water.[21] However, recent investigations have shown that the effect of water on the resin-dentin bond could be accelerated by water storage of the small 1x1 mm microbars used in the μTBS test.[22,23] It was assumed that water diffuses faster into the bonded interface of these small samples than into the interface of the larger samples of 3 to 4 mm diameter commonly used in shear tests. This idea of accelerated aging may be an option to evaluate bond durability of other adhesive joints too, like those with ceramic surfaces. An interesting matter in particular to study in this way is the stability of composites bonded to ceramic surfaces when hydrophilic multipurpose adhesives or hydrophobic adhesives are used. A greater stability for the latter is expected, as water would not be able to penetrate the adhesive interface.

The aim of this investigation was to evaluate μTBS and the bond durability of two resin cements, Tetric Flow and Nexus 2 after different time periods of water storage of the microbars, following: (1) ceramic surface treatment with HF or H₃PO₄ and, (2) application of hydrophilic or hydrophobic adhesives. In addition, the mode of failure was evaluated by stereomicroscopy and scanning electron microscopy (SEM).
4.3 Materials and methods

CEREC Vita blocs Mark II (fine-particle feldspar ceramic blocks, size 112; 12 x 10 x 15 mm Vita, Bad Säckingen, Germany), which are designed for the CEREC CAD/CAM system for the preparation of aesthetic restorations, were used as the ceramic to bond to. Fourteen of these blocks were selected. The surfaces to be bonded to were wet ground on a polishing machine (Buehler Ecomet V, Buehler Ltd, Lake Bluff, IL, USA) using 600 grit SiC paper. The blocks were then ultrasonically cleaned for 5 min in distilled water and air-dried.

Table 4.1 Combination of bonding agents and composite cements used in this study.

<table>
<thead>
<tr>
<th>Bonding agent / manufacturer</th>
<th>Criterium</th>
<th>Composition</th>
<th>Cement / manufacturer</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syntac Single-component batch: C25520 Vivadent/Schaan, Liechtenstein</td>
<td>Hydrophilic</td>
<td>Maleic acid, HEMA, methacrylate modified polyacrylic acid, initiators, stabilizers, water</td>
<td>Tetric Flow batch: C20284 Vivadent/Schaan, Liechtenstein</td>
<td>Bis-GMA, TEGDMA, Ba-Al-fluorosilicate glass and photoinitiators</td>
</tr>
<tr>
<td>OptiBond Solo Plus batch: 012851 Kerr Corp./Orange, CA, USA</td>
<td>Hydrophilic</td>
<td>Ethanol, Bis-GMA, GPDM, HEMA, silica, barium glass, sodium hexafluorosilicate</td>
<td>Nexus 2 batch: 101293 Kerr Corp./Orange, CA, USA</td>
<td>Monomers of methacrylic acid esters, Ba-Al-borosilicate glass, chemical and photoinitiators</td>
</tr>
<tr>
<td>Visio Bond batch: 0134 3M ESPE/Seefeld, FRG</td>
<td>Hydrophobic</td>
<td>Tricyclodecane diacrylate</td>
<td>Tetric Flow batch: C20284</td>
<td></td>
</tr>
<tr>
<td>Visio Bond batch: 0134 3M ESPE/Seefeld, FRG</td>
<td>Hydrophobic</td>
<td>Tricyclodecane diacrylate</td>
<td>Nexus 2 batch: 101293 Kerr Corp./Orange, CA, USA</td>
<td></td>
</tr>
</tbody>
</table>

\[ ^{a} \text{HEMA} = 2\text{-hydroxyethyl methacrylate; GPDM} = \text{glycerophosphate dimethacrylate; BIS-GMA} = \text{bisphenol A glycidyl methacrylate; TEGDMA} = \text{triethylene glycol dimethacrylate; UDMA} = \text{urethane dimethacrylate} \]
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Table 4.2 The fourteen bonding combinations to bond the cements Tetric Flow and Nexus 2 to each of the fourteen Vita blocks.

<table>
<thead>
<tr>
<th>Bonding strategy code</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Tetric Flow</td>
</tr>
<tr>
<td>HF/Si/-/TF</td>
<td>HF</td>
<td>silane</td>
<td>-</td>
<td>Tetric Flow</td>
</tr>
<tr>
<td>HF/Si/SSC/TF</td>
<td>HF</td>
<td>silane</td>
<td>Syntac Single-Component</td>
<td>Tetric Flow</td>
</tr>
<tr>
<td>HF/Si/VB/TF</td>
<td>HF</td>
<td>silane</td>
<td>Visio Bond</td>
<td>Tetric Flow</td>
</tr>
<tr>
<td>H₃PO₄/Si/-/TF</td>
<td>H₃PO₄</td>
<td>silane</td>
<td>-</td>
<td>Tetric Flow</td>
</tr>
<tr>
<td>H₃PO₄/Si/SSC/TF</td>
<td>H₃PO₄</td>
<td>silane</td>
<td>Syntac Single-Component</td>
<td>Tetric Flow</td>
</tr>
<tr>
<td>H₃PO₄/Si/VB/TF</td>
<td>H₃PO₄</td>
<td>silane</td>
<td>Visio Bond</td>
<td>Tetric Flow</td>
</tr>
<tr>
<td>No treatment</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Nexus 2</td>
</tr>
<tr>
<td>HF/Si/-/N2</td>
<td>HF</td>
<td>silane</td>
<td>-</td>
<td>Nexus 2</td>
</tr>
<tr>
<td>HF/Si/OBSP/N2</td>
<td>HF</td>
<td>silane</td>
<td>OptiBond Solo Plus</td>
<td>Nexus 2</td>
</tr>
<tr>
<td>HF/Si/VB/N2</td>
<td>HF</td>
<td>silane</td>
<td>Visio Bond</td>
<td>Nexus 2</td>
</tr>
<tr>
<td>H₃PO₄/Si/-/N2</td>
<td>H₃PO₄</td>
<td>silane</td>
<td>-</td>
<td>Nexus 2</td>
</tr>
<tr>
<td>H₃PO₄/Si/OBSP/N2</td>
<td>H₃PO₄</td>
<td>silane</td>
<td>OptiBond Solo Plus</td>
<td>Nexus 2</td>
</tr>
<tr>
<td>H₃PO₄/Si/VB/N2</td>
<td>H₃PO₄</td>
<td>silane</td>
<td>Visio Bond</td>
<td>Nexus 2</td>
</tr>
</tbody>
</table>

Note that Syntac Single-Component (SSC) and OptiBond Solo Plus (OBSP) are hydrophilic bonding agents and that Visio Bond (VB) is a hydrophobic bonding agent (silane agent was Monobond-s).

Bonding procedures

Before application of the two resin cements of Table 4.1 to each of the ceramic blocks, the ground ceramic surfaces to bond to were treated in one of the following ways:

   Treatment 1: no surface treatment.

   Treatment 2: freshly prepared 8 % HF was applied for 2 min, washed thoroughly for 1 min under tap water, dried with air and treated with silane primer Monobond-s (Vivadent, Liechtenstein) for 60 s and air-dried.

   Treatment 3: same as treatment 2, followed by the application of a thin layer of a hydrophilic bonding agent with a brush and then light cured for 20 s with a Translux CL (Kulzer & Co. GmbH, Wehrheim, Germany). A combination of bonding agent and resin cement from the same manufacturer was selected (Table 4.1).

   Treatment 4: same as treatment 2, followed by the application of a thin layer of a hydrophobic bonding agent with a brush and then light cured for 20 s. This bonding agent was used with both resin cements (Table 4.1).

   Treatment 5: 37 % H₃PO₄ was applied for 2 min, washed thoroughly for 1 min under tap water, dried with air and treated with silane primer for 60 s and air-dried.
Treatment 6: same as treatment 5, followed by the application of a thin layer of a hydrophilic bonding agent with a brush and then light cured for 20 s.

Treatment 7: same as treatment 5, followed by the application of a thin layer of a hydrophobic bonding agent with a brush and then light cured for 20 s.

An overview of the procedures is given in Table 4.2. The appearance of the ceramic surfaces after wet grinding (grit 600) or after treatment with 8% HF or 37% H$_3$PO$_4$ was studied by scanning electron microscope (Phillips SEM XL 20, Eindhoven, Holland).

The resin cement was applied and built-up in layers to a total thickness of 5 mm. Each layer was light cured for 40 s using the Translux CL (Kulzer & Co. GmbH, Wehrheim, Germany). The light power density was 400-450 mW/cm$^2$ measured with the Radiometer (Demetron Research Corp, Danbury, CT 06810).

**Microtensile bond strength test**

The built-up samples were stored in distilled water at 37°C for 1 d. Using a low speed cutting saw (Buehler Isomet 1000 Low Speed Saw, Buehler Ltd, Lake Bluff, IL, USA), each sample was cut into slabs of 1 mm thickness, starting at the cement side, through the ceramic block perpendicular to the bonded interface. The cutting advanced until 1 mm remained in order to keep the slabs fixed in position. The block of slabs was then rotated 90° and again cut perpendicular to the bonded interface to gain $1.0 \pm 0.1$ mm$^2$ rectangular microbars. During this second cutting procedure, premature debonding of the cement from the substrate occurred in a few cases, but for the untreated groups in all cases. From one block a maximum of 56 microbars could be obtained. Immediately after cutting (1 d samples), after one week (7 d samples) and four weeks (28 d samples) of water storage at 37°C, 10 microbars were randomly selected from each group and their cross-sectional area measured with a digital caliper (Mitutoyo Corp., Japan) before testing. The microbars were glued to the ACTA Microtensile testing device (Figure 3.1) by means of a light curing adhesive (Clearfil SE Bond, Kuraray Co., Japan). By using a universal testing machine (Model no. 6022; Instron, High Wycombe, Bucks, U.K.) at a cross head speed of 1 mm/min, a force was applied to the lower member of the device until failure.

To determine the mode of failure, all specimens were examined immediately after fracturing under a stereomicroscope. The fractured surfaces were classified according to one of the following types: A = adhesive failure at the ceramic-cement interface; B = cohesive failure in the ceramic; C = cohesive failure in the cement; D = mixed A and B and E = mixed A and C. For failure modes that could not be accurately established under the stereomicroscope, the surfaces were examined in the scanning electron microscope.
Statistical Analysis

Statistical analysis was carried out using SPSS statistical software package 9.01 (SPSS Inc., Chicago, IL, USA). Three-way analysis of variance was performed with the bond strength as the dependant variable. Ceramic surface treatment (HF or H$_3$PO$_4$), bonding agent (Syntac Single-Component, Optibond Solo Plus or Visio Bond), cement type (Tetric Flow or Nexus 2), and storage time (1 d, 7 d or 28 d) were treated as between subject factors. Whenever interaction or main effects were significant, they were further analyzed by tests of simple effect and tests of simple pairwise comparison. The groups that did not receive a surface treatment were not included in the analysis because no intact microbars could be obtained during the cutting procedure. Statistical significance was set at $\alpha = 0.05$ for all tests.

4.4 Results

The results of the three-way ANOVA revealed that there were statistically significant interactions between surface treatments, bonding agents, cement types and storage times ($P < 0.001$). The means and standard deviations of the $\mu$TBS of all tests are compiled in Tables 4.3 and 4.4.

Table 4.3 $\mu$TBS means and standard deviations for Tetric Flow cement at 1 day, 7 days and 28 days storage in water.

<table>
<thead>
<tr>
<th>Bonding strategy code</th>
<th>1 d $\mu$TBS MPa (sd)</th>
<th>7 d $\mu$TBS MPa (sd)</th>
<th>28 d $\mu$TBS MPa (sd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HF/Si/ - /TF</td>
<td>28.7 (5.9) $^a$</td>
<td>20.2 (4.3) $^b$</td>
<td>19.4 (2.7) $^b$</td>
</tr>
<tr>
<td>HF/Si/SSC/TF</td>
<td>24.7 (7.1) $^c$</td>
<td>13.5 (4.1) $^d$</td>
<td>12.3 (4.1) $^d$</td>
</tr>
<tr>
<td>HF/Si/VB/TF</td>
<td>18.2 (3.9) $^b$</td>
<td>21.0 (3.2) $^b$</td>
<td>21.5 (2.4) $^b$</td>
</tr>
<tr>
<td>H$_3$PO$_4$/Si/ - /TF</td>
<td>11.0 (2.6)</td>
<td>6 (2.3) $^e$</td>
<td>3.0 (2.0) $^e$</td>
</tr>
<tr>
<td>H$_3$PO$_4$/Si/SSC/TF</td>
<td>26.2 (3.7) $^{a,c}$</td>
<td>0.4 (1.3) $^f$</td>
<td>0 $^f$</td>
</tr>
<tr>
<td>H$_3$PO$_4$/Si/VB/TF</td>
<td>20.8 (4.2) $^b$</td>
<td>15.7 (3.4) $^d$</td>
<td>14.6 (2.0) $^d$</td>
</tr>
</tbody>
</table>

Note that Syntac Single-Component (SSC) is a hydrophilic and Visio Bond (VB) a hydrophobic bonding agent. (-): No microbars were available due to premature debonding during cutting. Data in rows or columns with the same superscript letters are not significantly different ($P > 0.05$).
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Table 4.4 μTBS means and standard deviations for Nexus 2 cement at 1 day, 7 days and 28 days storage in water.

<table>
<thead>
<tr>
<th>Bonding strategy code</th>
<th>1 d μTBS MPa (sd)</th>
<th>7 d μTBS MPa (sd)</th>
<th>28 d μTBS MPa (sd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HF/Si/-/N2</td>
<td>24.3 (3.1)*</td>
<td>24.7 (4.2)*</td>
<td>22.8 (3.3)*</td>
</tr>
<tr>
<td>HF/Si/OBSP/N2</td>
<td>36.6 (6.5)</td>
<td>17.7 (3.5) b,d</td>
<td>15.6 (4.9) b</td>
</tr>
<tr>
<td>HF/Si/VB/N2</td>
<td>17.0 (5.4) d</td>
<td>18.9 (2.4) d</td>
<td>20.2 (3.9) a,d</td>
</tr>
<tr>
<td>H₃PO₄/Si/-/N2</td>
<td>7.2 (3.0)</td>
<td>4.8 (2.5) e</td>
<td>1.4 (2.1)</td>
</tr>
<tr>
<td>H₃PO₄/Si/OBSP/N2</td>
<td>25.2 (4.6) *</td>
<td>8.1 (4.1) e</td>
<td>5.7 (2.5) e</td>
</tr>
<tr>
<td>H₃PO₄/Si/VB/N2</td>
<td>18.7 (4.3) d</td>
<td>17.4 (4.1) d</td>
<td>16.8 (2.8) b,d</td>
</tr>
</tbody>
</table>

Note that OptiBond Solo Plus (OBSP) is a hydrophilic and Visio Bond (VB) a hydrophobic bonding agent. (-): No microbars were available due to premature debonding during cutting. Data in rows or columns with the same superscript letters are not significantly different (P > 0.05).

1-day bond strength

The results of the 1 d bond strength show that the μTBS for groups that received a H₃PO₄ surface treatment (H₃PO₄/Si/-/TF and H₃PO₄/Si/-/N2) was lower than for groups treated with HF (HF/Si/-/TF and HF/Si/-/N2) for both cements tested (P < 0.001). For the H₃PO₄-treated groups the bond strengths were significantly higher when intermediate bonding agents were used (H₃PO₄/Si/SSC/TF, H₃PO₄/Si/VB/TF, H₃PO₄/Si/OBSP/N2 and H₃PO₄/Si/VB/N2) compared to direct application to H₃PO₄-treated surfaces (H₃PO₄/Si/-/TF and H₃PO₄/Si/-/N2) for both cements tested (P < 0.001). For these groups the bond strength was statistically higher with the hydrophilic bonding agents Syntac Single-Component and OptiBond Solo Plus (H₃PO₄/Si/SSC/TF and H₃PO₄/Si/OBSP/N2) than with the hydrophobic bonding agent Visio Bond (H₃PO₄/Si/VB/TF and H₃PO₄/Si/VB/N2) (pairwise comparisons with P = 0.002 for Tetric Flow cement and p < 0.001 for Nexus 2 cement). On the other hand, the HF-treated groups with Visio Bond (HF/Si/VB/TF and H₃PO₄/Si/VB/N2) exhibited lower mean μTBS compared to HF-treated groups with and without Syntac Single-Component or OptiBond Solo Plus (HF/Si/SSC/TF and H₃PO₄/Si/OBSP/N2 respectively HF/Si/-/TF and H₃PO₄/Si/-/N2) for both cements (pairwise comparisons with P < 0.001). The results also showed that the highest mean μTBS at the 1 d storage period was obtained with Nexus 2 cement after surface treatment with HF and applying OptiBond Solo Plus (36.6 MPa).
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Table 4.5 Percentage of all examined microbars counted for each of the failure modes after 1 day, 7 days and 28 days testing periods.

<table>
<thead>
<tr>
<th>Type of failure</th>
<th>1 d (%)</th>
<th>7 d (%)</th>
<th>28 d (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A = adhesive: ceramic-cement</td>
<td>60.0</td>
<td>85.8</td>
<td>94.2</td>
</tr>
<tr>
<td>B = cohesive: ceramic</td>
<td>0.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C = cohesive: cement</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>D = mixed A and B</td>
<td>17.5</td>
<td>5.8</td>
<td>2.5</td>
</tr>
<tr>
<td>E = mixed A and C</td>
<td>21.7</td>
<td>8.3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Bond durability

Tests of simple time within cement within treatment within bonding agent for Tetri c Flow cement revealed that the bond strengths were stable during water storage for the HF-treated group with Visio Bond only (HF/Si/VB/TF), whereas for Nexus 2 cement bond strengths were stable for HF/Si/-/N2, HF/Si/VB/N2 and H₃PO₄/Si/VB/N2. During the water storage the bond strength decreased for both the HF and H₃PO₄ surface treatments with both hydrophilic bonding agents Syntac Single-Component and OptiBond Solo Plus (HF/Si/SSC/TF, HF/Si/OBSP/N2, H₃PO₄/Si/SSC/TF and H₃PO₄/Si/OBSP/N2) (pairwise comparisons significant with \( P < 0.001 \)).

Table 4.6 Percent (%) adhesive failures found after fracture of the different bonding strategies for Tetri c Flow and Nexus 2 after 1 day, 7 days and 28 days water storage.

<table>
<thead>
<tr>
<th>Code</th>
<th>Tetri c Flow</th>
<th>Nexus 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/Si/-/TF</td>
<td>10 80 90</td>
<td>10 40 60</td>
</tr>
<tr>
<td>HF/Si/SSC/TF</td>
<td>40 40 100</td>
<td>40 100 100</td>
</tr>
<tr>
<td>HF/Si/VB/TF</td>
<td>90 80 90</td>
<td>90 90 100</td>
</tr>
<tr>
<td>H₃PO₄/Si/-/TF</td>
<td>100 100 100</td>
<td>100 100 100</td>
</tr>
<tr>
<td>H₃PO₄/Si/SSC/TF</td>
<td>100 100 100</td>
<td>100 100 100</td>
</tr>
<tr>
<td>H₃PO₄/Si/VB/TF</td>
<td>100 100 100</td>
<td>100 100 90</td>
</tr>
</tbody>
</table>

The changes in failure modes during the three testing periods are shown in Table 4.5. The highest detected failure mode after 1 d testing was the adhesive type of failure (60.0 %). After 28 d water storage the percentage of adhesive failures increased to 94.2. Table 4.6 shows the distribution of adhesive failures after the different surface treatments for the Tetri c Flow and Nexus 2 cement at the three testing periods. The H₃PO₄-treated groups and groups with Visio Bond bonding agent exhibited the highest percentage of adhesive failures after the 1 d testing.
For groups with the Syntac Single-Component and OptiBond Solo Plus bonding agents there were an increased percentage of adhesive failures that reached 100% after 28 d of water storage.

Figure 4.1a - c show the scanning electron micrographs of the Vitablocs Mark II ceramic surface after wet grinding with grit 600 SiC paper, after treating with 37% H₃PO₄ and after treating with 8% HF respectively.

4.5 Discussion

This laboratory study was designed to investigate the influence of two main parameters on bond strength and bond durability of two low viscosity resin composite cements bonded to ceramic. The first was the type of acidic conditioner used, which was either HF or H₃PO₄, and the second was the nature of the intermediate bonding agent used (hydrophilic or hydrophobic bonding agents) to facilitate bonding to the ceramic surface. Silanization of the acid treated ceramic surfaces prior to applying the adhesives or cements was used as a standard procedure as its importance in bond formation has been well established.[16,17,19]
The μTBS test used for bond strength testing offered several advantages compared to the conventional shear and tensile strength tests in terms of producing more adhesive failures and supplying multiple specimens from cutting one large sample.[24,25] Another advantage of this methodology is that it provides an opportunity to test the influence of water on resin-ceramic bond durability in an accelerated way by storing the small 1x1 mm microbars in water for a period of time prior to testing.[23,26] The small dimensions of the microbars require less time for water infiltration into the adhesive interface than the larger samples would do, used in the conventional shear or tensile test.

Examination of the modes of failure of the 1 d samples revealed that the adhesive interface was always involved in the fractures with only one exception of a cohesive fracture in the bulk of the ceramic (Table 4.5). This result is in accordance with what one would expect of microbars loaded in tension as they allow a homogeneous distribution of the applied stresses close to the adhesive interface.[27] The predominant mode of failure for the 1 d samples was adhesive (60.0 %). This percentage increased to 85.8 after the first week of water storage and to 94.2 after 28 d. This rapid increase in number of adhesive failures in a relatively short period of time demonstrates the accelerated deterioration effect of water on bond strength for small specimens like the microbars.

The results of this study support the importance of HF etching prior to bonding composite cements directly to a ceramic surface. Low bonds were obtained if the cements were applied without any treatment of the ceramic surface or after treatment with H₃PO₄ (Tables 4.3 and 4.4). All untreated samples showed debonding already during the cutting procedure in making the microbars, whereas the H₃PO₄ treatment without an intermediate bonding agent showed significantly lower bond strength values than the HF treatment, which confirms the findings in earlier studies.[15,28] In all cases of H₃PO₄ treatment without an intermediate bonding agent, the mode of failure was adhesive (Table 4.6). The large difference in bond strength between HF and H₃PO₄-treated surfaces is explained by the large difference in surface texture. HF is capable of creating numerous undercuts and surface pits (Figure 4.1c) by preferential dissolution of the glass phase of the ceramic matrix [29], which leads to a dramatic increase of the surface area to be silanized and to the possibility of micromechanical attachment. The action of H₃PO₄ is limited to clean the porcelain surface; SEM micrographs indeed revealed that H₃PO₄ only exposes surface porosities and defects without any apparent etching pattern (Figure 4.1b). Yet H₃PO₄ does chemically alter the surface by neutralizing the alkalinity of the adsorbed water layer, which is present on all ceramic restorations and thereby enhances the chemical activity of the silane primer subsequently applied.[30]
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Application of an intermediate layer of Syntac Single Component or OptiBond Solo Plus to both HF and H_3PO_4-treated ceramic resulted in a substantial increase in bond strength for both resin cements (Tables 4.3 and 4.4). The increase is thought to be attributed to the better wetting by the low viscosity bonding agents to the ceramic surface, which enables a more efficient involvement of the C=C-bonds of the silane in the bonding reaction. An exception formed the combination HF/Si/SSC/TF, where the application of Syntac Single Component did not increase the bond strength (Table 4.3). A clear explanation cannot be given, but it might be that values between 25 and 29 MPa are close to the maximum bond strength for Tetric Flow and cannot become higher.

In addition the higher wetting capability of the bonding agent could bring about reduction in number and size of the flaws at the adhesive interface.[31] A similar result was also reported by previous shear bond strength study of orthodontic brackets bonded to porcelain.[32]

Application of an intermediate layer of Visio Bond showed a substantial increase in bond strength for both resin cements only to H_3PO_4-treated surfaces and not to HF-treated surfaces (Tables 4.3 and 4.4). The results also showed that the 1 d bond strength values for Visio Bond as an intermediate resin was consistently lower than with Syntac Single Component or OptiBond Solo Plus regardless the surface treatment (HF or H_3PO_4) or resin cement used (Tetric Flow or Nexus 2). The most probable explanation for this interesting finding is a decreased possibility for the Visio Bond monomer Tricyclodecane diacrylate to react with the silane-C=C-bonds by severe steric hindrance. The reactive C=C-bonds are too closely positioned to this bulky monomer (Figure 4.2), that they cannot easily reach the silane-C=C-bonds to react with.Synthesis of a similar monomer with longer chains carrying the C=C-groups may significantly improve coupling to the silane layer. Because of its high water stability, as will be discussed later, these type of intermediate bonding agents may have a great potential in durable porcelain repairs.

It should be noted that the 1 d bond strength values are representing data of microbars that had been exposed to water at varying degree, as water could only partially diffuse into the bonded blocks until the moment of cutting.

Several reports are available on the influence of water on the durability of resin-ceramic bond strength.[33-38] Most of them reported a decrease in bond strength after long-term water storage, which is believed to be the result of hydrolysis of the silane bond.[39] With respect to silane treatment, many efforts were made to improve the effectiveness of the silane primer by using either multicomponent silane primers instead of the prehydrolyzed single component silane

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primers [17,40], or by eliminating water and other contaminants from the silane treated surface through heat treatment.[19,41]

Less attention however, has been given to investigate the role of the resin cement or intermediate bonding agent in bond durability. The present results show that resin-ceramic bond durability strongly depended on the resin cement. When Nexus 2 was applied directly to the HF-treated ceramic surface the bond was stable during a period of 28 d of water storage (Table 4.4). Tetric Flow on the other hand showed a significant reduction of 32 % in bond strength after 28 d of water storage (Table 4.3). The decreased stability can be attributed to two causes related to water sorption namely hydrolysis of the Si-O-bonds and swelling. If Tetric Flow has a (slightly) greater affinity for water sorption than Nexus 2 by their compositional differences, then the Si-O-bonds of Tetric Flow will be sooner exposed to hydrolytic action. At the same time there will also be (slightly) more swelling of the cement, which will increase shear stresses in the adhesive interface that weakens the bond. For both resin cements swelling may be the explanation for the rapid loss of bond strength when they were applied directly to the less retentive H3PO4 treated surfaces (Table 4.3 and 4.4).

The present results also showed a strong dependence of bond durability on the nature of the intermediate bonding agent. Dramatic differences were observed between Syntac Single Component and OptiBond Solo Plus on the one hand and Visio Bond on the other. Although application of Syntac Single Component and OptiBond Solo Plus significantly enhanced the bond strength for the two cements in most cases, the water stability was poor. A sharp decrease occurred after 28 d water storage for both resin cements and both acid treatments, while Visio Bond formed stable combinations (Tables 4.3 and 4.4). Only the combination H3PO4/Si/ VB/TF showed 30 % reduction in bond strength, but this was significantly lower than the 100 % reduction in bond strength for the combination H3PO4/Si/SSB/TF. The rapid deterioration of the bond when using Syntac Single Component or OptiBond Solo Plus is strongly connected to the hydrophilic character of these bonding agents. Both contain polymers with hydrophilic moieties and polymers that are formed from hydrophilic monomers like 2-hydroxyethyl methacrylate (HEMA) [42], Glycerophosphate dimethacrylate (GPDM), Maleic acid or various other alkenoic acids, which allow considerable water uptake. As discussed above for the two resin cements Tetric Flow and Nexus 2, water uptake will weaken the bond by hydrolysis of the Si-O-bonds and water swelling. Because Syntac Single Component and OptiBond Solo Plus take-up water easily, the effect of water swelling will seriously stress the bond at the adhesive interface and will play an important role in weakening the adhesive joint.
In a recent investigation by Foxton et al. [43], where the same methodology was used for testing the durability of resin-ceramic bonds, the authors also found a negative effect on bond durability when using multicomponent ceramic primer/bonding agents. This was attributed to the water contained as a solvent within the bonding agents. However, we do believe that the hydrophilic character of the bonding system is the main cause for bond strength reduction, as our results have shown that the bond stability was affected for both, the water based Syntac Single Component adhesive and the ethanol based OptiBond Solo Plus adhesive.

Additional weakening of the adhesive joint may come from alteration of mechanical properties of these bonding agents caused by leaching out of uncured water-soluble monomers and low molecular weight oligomers. [44] Hogan et al. [45] determined the cohesive strength of several other dentin bonding agents after long term air or water storage in a microtensile test setup and found a significant decrease in tensile strength of these materials after water storage.

Visio Bond, in contrast to Syntac Single Component and OptiBond Solo Plus, has marked hydrophobic properties, as it solely consists of a tricyclic aliphatic diacrylate monomer, a saturated hydrocarbon with two acrylate groups (Figure 4.2). Its hydrophobic character has been demonstrated by Feilzer et al. [46] in experiments of stress relaxation of various resin composites by water sorption. They found that all composites based on BIS-GMA/TEGDMA and UEDMA (urethane dimethacrylate) monomers fully relaxed, while a composite based on tricyclocdecane diacrylate allowed very little hygroscopic expansion. The impermeability for water protects the silane bond at the resin-ceramic interface and prevents water swelling. This
explains the better water stability of joints with Visio Bond as an intermediate resin. It is interesting to note that there was a tendency, although not significant, for a gradual increase in bond strength with time when Visio Bond was applied to the HF-treated surfaces (HF/Si/VB/TF and HF/Si/VB/N2). This was not seen for Visio Bond applied to the less retentive H₃PO₄-treated surfaces (H₃PO₄/Si/VB/TF and H₃PO₄/Si/VB/N2). The surface texture after a H₃PO₄ treatment hardly shows possibilities for mechanical retention (Figure 4.1b) as compared to a HF treatment (Figure 4.1c). Thurmond et al. [28] demonstrated earlier the importance of mechanical retention for bond strength durability of resin composites bonded to porcelain. Apparently, if conditions are met for sufficient (micro) mechanical retention and for a stable bond, the bond may even mature in due time.

We speculated earlier that the bond strength with monomers like that of Visio Bond could be improved if the two functional C=C-groups would be placed on longer chains, further away from the tricyclic aliphatic diacrylate structure for more effective coupling with the silane-C=C. Combined with the high water stability, such monomers would be promising bonding agents in porcelain repair. Also composites based on this monomer when applied directly to HF and silanized porcelain surfaces could be an option for strong repairs.

From the present study it can be concluded that strong and durable bonds to ceramics can be obtained with resin cements and in particular those of hydrophobic nature, when these are applied directly to HF etched and silanized surfaces. The use of intermediate bonding agents improves the bond strength, however in water the current hydrophilic bonding agents rapidly lose strength due to water sorption. Hydrophobic bonding agents show stable bonds in water, but the particular bonding agent investigated in this study needs a change of molecular structure to improve the bond strength.

4.6 References

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