Effect of Hydrofluoric Acid Etching on Shear Bond Strength of an Indirect Resin Composite to an Adhesive Cement

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INTRODUCTION

In dentistry today, resin composite materials are highly esteemed because of these unanimously acclaimed advantages: superior esthetic quality, high mechanical strength, ease of application, and cost-effectiveness.

Recently, highly filled composites have been developed for clinical applications and they possess high mechanical strength and wear resistance close to those of ceramics¹⁻⁵. In light of these qualities, it is possible to use them for indirect restorations such as inlays, onlays, jacket crowns, and even fixed partial dentures. However, clinicians often encounter crack formation and bulk fracture of composite restorations due to brittleness of composite materials. Clinical success of these systems is reliant upon an adequate bond of the resin cement to the resin composite restoration as well as to the tooth structure.

In general, bonding between two composite layers is achieved in the presence of an oxygen-inhibited layer of unpolymerized resin⁶. As indirect restorations and aged direct restorations do not contain an unpolymerized surface layer, several techniques have been suggested to improve the composite-composite bond⁷⁻²⁰. Three possible mechanisms of bonding two composite layers are namely, chemical bonding to the resin matrix, chemical bonding to the exposed filler particles, and micromechanical retention caused by penetration of the resin cement into microcracks in the resin matrix⁷.

Mechanical retention can be achieved by airborne particle abrasion⁷⁻¹⁴, roughening with diamond points or carbide burs¹⁵, acid etching with phosphoric acid (PA)¹⁶⁻¹⁸, acidulated phosphate fluoride (APF)¹³,¹⁵, or hydrofluoric acid (HF)⁷⁻¹⁵,¹⁷⁻²⁰. As for chemical bonding, it is based on the principle of improving adhesion between resin and SiO₂ filler by using silane coupling agents⁸⁻¹⁴,¹⁷⁻²⁰, silica coating¹⁵,¹⁶ and infiltration of resin monomers into composites.

In particular for the HF acid, both positive¹¹,¹⁸,²⁰ and negative¹²⁻¹⁵,¹⁷,²⁰ effects on the bonding of filled composites¹¹,¹⁵ and indirect resin composites¹²,¹³,¹⁷,¹⁸,²⁰ have been reported using different acid concentrations and varied etching times. These widely varied bond strengths may be attributed to the different compositions of resin composites used in each study. Besides, Trajtenberg et al.¹⁹ suggested that the presence of a high percentage of glass fillers (claimed to be 75–85% by manufacturer) makes a good candidate for etching with hydrofluoric acid.

Among the numerous indirect resin composites, Estenia C&B was introduced into clinical use as a hybrid ceramic—which can be used even for posterior restorations⁸. Since Estenia C&B is loaded with a total 92 wt% of fillers including 76 wt% of highly etchable glass fillers²⁻⁴, it should be presumably suitable for HF acid etching. However, the effect of HF etching on the bonding of adhesive resin cements to Estenia C&B has not been clarified.
yet.

It is hypothesized that HF acid treatment would produce mechanical retention by dissolving etchable glass filler particles, and that this phenomenon could enhance the bonding of adhesive cements to Estenia C&B.

The purpose of this study was to evaluate the effect of 1% HF acid treatment on the bonding of adhesive cement Panavia F 2.0 to indirect resin composite Estenia C&B after thermocycling. Results thereof were then compared with those of airborne particle abrasion.

MATERIALS AND METHODS

Materials

Materials used in this study are listed in Table 1. An indirect resin composite, Estenia C&B (Kuraray Medical Inc., Tokyo, Japan), which is categorized as a hybrid composite was selected as the substrate. This material contained approximately 92 wt% inorganic fillers in a polymerizable tetrafunctional urethane methacrylate. The filler particles consisted of 16% ultrafine alumina particles (average particle size of 20 nm) and 76% fine alumino-silicate glass particles (average particle size of 1.5 μm).

Panavia F 2.0 (Kuraray Medical Inc.) was used as the adhesive cement. Panavia F 2.0 is a dual-cure adhesive system containing 10-methacryloyloxydecyl dihydrogen phosphate (MDP) as the adhesive functional monomer. A mixture of Clearfil Porcelain Bond Activator (Kuraray Medical Inc.), which contained 3-methacryloxypropyl trimethoxysilane (γ-MPTS), and Clearfil New Bond (Kuraray Medical Inc.) was used as the silane primer.

Shear bond testing

Pairs of resin composite disk specimens (10 and 8

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Materials used</th>
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<tbody>
<tr>
<td>Material</td>
<td>Product name</td>
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<tr>
<td>Indirect resin composite</td>
<td>Estenia C &amp; B (DA2)</td>
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<tr>
<td>Adhesive cement</td>
<td>Panavia F 2.0</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td>Silane-coupling agent</td>
<td>Clearfil Porcelain Bond Activator</td>
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<tr>
<td></td>
<td>Clearfil New Bond</td>
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UDMA: Urethane dimethacrylate
UTMA: Urethane tetramethacrylate
MDP: 10-methacryloyloxydecyl dihydrogen phosphate
Bis-GMA: 2,2-bis [p-(2'-hydroxy-3'-methacryloxypropoxy) phenyl] propane
HEMA: 2-hydroxyethyl methacrylate

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Surface pretreatment methods</th>
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<tr>
<td>Code</td>
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<tr>
<td>NT</td>
<td>No surface treatment</td>
</tr>
<tr>
<td>AP</td>
<td>Air-borne particle abrasion using 50 μm aluminum oxide at 0.2 MPa</td>
</tr>
<tr>
<td>E30s</td>
<td>Etched with 1% HF solution for 30 sec</td>
</tr>
<tr>
<td>E5m</td>
<td>Etched with 1% HF solution for 5 min</td>
</tr>
<tr>
<td>E10m</td>
<td>Etched with 1% HF solution for 10 min</td>
</tr>
<tr>
<td>SC</td>
<td>Silane-coupling (Clearfil New Bond + Clearfil Porcelain Bond Activator)</td>
</tr>
<tr>
<td>AP/SC</td>
<td>Air-borne particle-abrasion using 50 μm aluminum oxide at 0.2 MPa + Silane-coupling</td>
</tr>
<tr>
<td>E5m/SC</td>
<td>Etched with 1% HF solution for 5 min + Silane-coupling</td>
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mm in diameter by 3 mm thickness) were prepared. Resin paste was packed into a Teflon mold between two microscope glass slides, and light-exposed for five minutes from both sides using a photo-polymerization unit (α-LITE II, J. Morita Corp., Suita, Japan). Then, specimens were heat-cured for 15 minutes at 110°C using a heat-curing unit (KL-310, Kuraray Medical Inc., Tokyo, Japan).

The disk surfaces to be bonded were ground with a 600-grit silicon carbide abrasive paper, followed by one of the eight procedures listed in Table 2. Airborne particle abrasion was carried out using 50-μm aluminum oxide (50-micron Aluminum Oxide, Jelenko, New York, NY, USA) at 0.2 MPa for five minutes. Hydrofluoric acid treatment was achieved by soaking in 1% HF solution for one of the three soaking times — 30 seconds, five minutes, and 10 minutes. Then, specimens were rinsed under running water and ultrasonically cleaned in distilled water for five minutes. The silane primer was applied for 10 seconds, gently air-blasted, and heated at 110°C for one minute using a heat-curing unit (KL-310).

A piece of tape (0.03 mm thickness) with a 5.0-mm-diameter opening was placed on the treated surface to provide a bonding area. Adhesive specimens were fabricated by bonding a pair of pretreated resin composite disks with an adhesive cement (Panavia F 2.0), then light-cured for 20 seconds using a LED curing light (G-Light, GC Corp., Tokyo, Japan). Fourteen specimens were fabricated for each surface treatment group, and stored in 37°C distilled water for 24 hours. Each group was subdivided into two thermocycling treatment groups (n=7). One group was not thermocycled, while the other group was subjected to thermocycling for 50,000 cycles between 4°C and 60°C water baths with 1-minute dwell time at each temperature. Therefore, a total of 112 specimens for 14 groups, including two thermocycling treatment groups for eight surface pretreatment groups, were fabricated.

Shear bond strength was determined using a universal testing machine (AGS-5kNG, Shimadzu Corp., Kyoto, Japan) at a crosshead speed of 1.0 mm/min. Figure 1 is a schematic illustration of the specimen for shear bond testing.

Debonded surfaces were gold-coated using an ion sputtering device (Fine Coat Ion Sputter JFC-1100, JEOL, Tokyo, Japan), and then observed under a scanning electron microscope (SEM) (JSM-1100, JEOL) to assess the failure mode. In addition, the surface textures of airborne particle-abraded (group AP) and HF-etched (groups E30s, E5m, E10m) Estenia C&B specimens were also observed.

### Statistical analysis
Shear bond strengths of all treatment groups were analyzed with two-way analysis of variance (ANOVA) using the number of thermocycles and surface pretreatment as independent factors. Multiple comparisons between each group were performed using two-way ANOVA and Bonferroni’s test at 95% confidence level.

### RESULTS

Figure 2 summarizes the effects of surface pretreatments for mechanical retention on shear bond strength to the composite material. As revealed by two-way ANOVA, significant differences in bond strength were found between pre- and post-thermocycling groups (P<0.0001) and among the different surface pretreatment groups (P<0.0001). Interaction between thermocycling and surface pretreatment was also significant (P=0.0004). Average bond strength before thermocycling varied from 11.8 to 17.9 MPa. The composite material etched with 1% HF for five minutes (category b) showed significantly greater bond strength than the ground composite material (category a). Average bond strength after thermocycling varied from 4.7 to 18.3 MPa. Application of 50,000 thermocycles divided the bond strengths into three categories. Post-thermocycling bond strength of etched composite (category C) was greater than that of ground composite (category A). The difference between grinding and airborne particle abrasion was not significant (category a for pre-thermocycling and category A for post-thermocycling). For the three etched groups, bond strength was not significantly reduced by application of thermocycling (P>0.05).

Figure 3 shows the effects of airborne particle abrasion, silane coupling, and their combination on shear bond strength to the composite material. Significant differences in bond strength were found between pre- and post-thermocycling groups (P=0.0005) and among the different surface pretreatment groups (P<0.0001), as demonstrated by two-way ANOVA. Interaction between thermocycling
and surface pretreatment was also significant (P=0.015). Average bond strength before thermocycling varied from 11.8 to 16.3 MPa, and no significant differences in bond strength were found among the four groups (category c). Average bond strength after thermocycling varied from 4.7 to 14.3 MPa. Application of 50,000 thermocycles divided the bond strengths into two categories. After thermocycling, the bond strength of airborne particle-abraded and silane-treated composite (AP/SC, category E) was greater than that of airborne particle-abraded composite (AP, category D). As for the two silane-treated groups (SC and AP/SC), bond strength was not significantly reduced (P>0.05) with application of thermocycling.

Figure 4 shows the effects of HF etching, silane coupling, and their combination on shear bond strength to the composite material. As revealed by
two-way ANOVA, there were significant differences in bond strength between pre- and post-thermocycling groups (P<0.0001) and among the different surface pretreatment groups (P<0.0001). Interaction between thermocycling and surface pretreatment was also significant (P=0.037). Average bond strength before thermocycling varied from 11.8 to 19.1 MPa. Two groups etched with 1% HF for five minutes (category e) showed significantly greater bond strength than the ground composite material (category d). Average bond strength after thermocycling varied from 4.7 to 18.3 MPa. Application of 50,000 thermocycles divided the bond strengths into three categories. After thermocycling, the bond strength of composite etched with 1% HF for five minutes (category H) exhibited the greatest bond strength. The value of 18.3 MPa was significantly greater than those of ground composite (category F) and two silane-treated composites (SC and E5m/SC, category G). The bond strengths of two groups (SC and E5m) were not significantly reduced by application of thermocycling (P>0.05).

Figure 5 compares the effect of etching alone (1% HF etching for five minutes) and sandblasting-silane combination on shear bond strength to the composite material. As revealed by two-way ANOVA, significant differences in bond strength were found between pre- and post-thermocycling groups (P=0.0005). No significant differences, however, were found between the two surface conditions (P=0.8778). Interaction between thermocycling and surface pretreatment was also not significant (P=0.473). Although pre-thermocycling bond strengths were at an identical level (category f), the etched group demonstrated greater post-thermocycling bond strength (category J) than the silane-treated group (category I). In addition, the bond strengths of both groups were not reduced after application of 50,000 thermocycles (P>0.05).

In terms of surface texture, airborne particle-abraded surface was roughened by alumina particles such that the distinction between the filler particles and resin matrix became eroded (Fig. 6). As for the effect of 1% HF etching, it is shown in Fig. 7. SEM observation revealed that the HF solution dissolved the filler particles of resin composite and consequently produced a porous irregular surface. In addition, the extent of dissolution of filler particles increased with the soaking time in HF solution (Fig.

![Fig. 6](image6.png) SEM micrograph of Estenia C&B after airborne particle abrasion.

![Fig. 7](image7.png) SEM micrographs of Estenia C&B exposed to 1% HF solution for: (a) 30 sec; (b) 5 min; and (c) 10 min.
Figures 8(a) and (b) show the debonded surfaces of groups AP and E5m after thermocycling. By means of SEM analysis, most of the specimens showed mixed adhesive-cohesive type of failure, with the exception of adhesive failure for non-treated group (group NT). In Group AP, it was chiefly mixed failure: adhesive failure at the bonding interface and cohesive failure of adhesive cement which had penetrated the pits formed by airborne particle abrasion. Similarly, group E5m also showed mixed failure, with cohesive failure in the resin matrix of resin composite and cohesive failure of adhesive cement which had penetrated the voids. The latter were produced due to the dissolution of filler particles during soaking in HF solution.

DISCUSSION

The hypothesis of this study was accepted, because HF acid treatment significantly enhanced the bonding of adhesive cement to Estenia C&B. When Estenia C&B was exposed to HF acid, a water monolayer penetrated the voids to the filler. This, in turn, disorganized the silane layer which was responsible for stabilizing the glass filler-resin interface. Furthermore, the HF acid dissolved the glass filler particles. Put together, all these mechanisms weakened the filler particle-matrix interface and led to filler dissolution.

For the HF acid-treated specimens, the resin cement penetrated the voids and produced micromechanical interlocking—thereby achieving the required bonding between resin cement and indirect composite. As for airborne particle abrasion, it also roughened the composite. However, the degree of concavity and convexity of airborne particle-abraded surface seemed lower than that of HF-treated surfaces (Figs. 6 and 7). Further, as shown in Fig. 2, groups E5m and E10m revealed higher bond strengths compared to airborne particle-abraded specimens (group AP) after thermocycling. Taken together, these results could be attributed to the aforementioned morphological disparity.

Many studies have reported on both the positive and negative effects of HF etching on the bonding of resin composites. Some studies have also reported that bond strength was not affected by etchant concentration and/or etching time. Results of this study agreed with the latter reports. Although group E5m showed the highest bond strength, it was not significantly different from the other two HF-etched groups both before and after thermocycling (Fig. 2). In the present study, a comparatively longer etching time was required as compared to previous studies due to the low concentration of HF solution employed.

For most of the new-generation silane coupling systems, they are composed of two or three solutions. One is the silane coupler, and the other is the acid component of the solution which enhances the formation of siloxane bonds. Papacchini et al. have reported on a three-component system, which was a combination of the silane coupler with a two-step total-etch adhesive as the acidic component. Superior repair strength was obtained with a microhybrid resin composite when compared to pre-hydrolyzed and two-component silane primers. In addition, heat treatment has been employed to accelerate the chemical interaction between the silane molecules and the inorganic surface. For these reasons, the silane coupling procedure was carried out using a three-component system and heat treatment.

Effects of silane coupling agent differed with the
surface pretreatment method (Figs. 3 and 4). Silane coupling agents form chemical bonds between glass filler particles and resin matrix during polymerization. The silanol group of a silane molecule reacts with silica on the glass filler surface, and the methacrylate group in silane molecule forms a covalent bond with the resin matrix. In the present study, glass filler particles were exposed on the airborne particle-abraded surface. Consequently, group AP/SC exhibited a higher bond strength compared to group AP after thermocycling (Fig. 3). On the other hand, the methacrylate group did not react with the polymerized resin matrix. With HF etching, a porous resin matrix surface was obtained due to the loss of glass filler particles (Fig. 7). Therefore, the bond strength of group E5m/SC was significantly decreased after thermocycling (Fig. 4).

Estenia C&B contained alumina particles, which were not degraded by HF acid nor reacted with the silane coupler27-29. This claim was confirmed by means of SEM analysis (Fig. 7). Panavia F 2.0 penetrated the voids formed by HF etching with involving alumina particles. Consequently, a mechanical interlocking layer of higher cohesive strength was obtained for group E5m. This phenomenon was confirmed by the SEM analysis of failure mode for group E5m. Failed Estenia C&B substrate showed a concave surface which indicated the boundary of the mechanical interlocking layer (Fig. 8(b)).

In clinical dentistry today, airborne particle abrasion followed by application of silane coupling agent is a well-known and recommended method7,8,10,12,13,20. However, results of this study showed that 1% HF etching for five minutes (group E5m) was more effective for the bonding of Panavia F 2.0 to Estenia C&B after thermocycling as compared to group AP/SC (Fig. 5).

Nonetheless, airborne particle abrasion may be indicated for intraoral repair of fractured resin composites, although it is not suitable for final insertion of indirect resin composite restorations due to the possibility of marginal damage30. HF acid treatment will be superior to airborne particle abrasion where there is no indication for specific instruments such as sandblaster or compressed air.

Considering the hazardous effects of HF solution, it is recommended that HF be applied as a gel material to prevent its volatilization or dripping. In this context, the appropriate etching time and acid concentration will vary. Besides, the etching time of five minutes may be too impractically long for clinical use. Therefore, further investigations on HF acid concentration and etching time should be carried out to obtain clinically acceptable procedures.


