Chapter 5

Effect of Three Surface Conditioning Methods to Improve Bond Strength of Particulate Filler Resin Composites

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Effect of Three Surface Conditioning Methods to Improve Bond Strength of Particulate Filler Resin Composites

M. Özcan\textsuperscript{a}, P.K. Vallittu\textsuperscript{b}, P. Alander\textsuperscript{b}, M-Ch. Huysmans\textsuperscript{a}, W. Kalk\textsuperscript{a}

\textsuperscript{a}University of Groningen, Faculty of Medical Sciences, Department of Dentistry and Dental Hygiene, Groningen, The Netherlands.
\textsuperscript{b}University of Turku, Institute of Dentistry, Department of Prosthodontics and Biomaterials Research, Turku, Finland.

ABSTRACT

The objective of this study was to evaluate the effect of three surface conditioning methods on the shear bond strength of a particulate filler resin-composite (PFC) to 5 PFC substrates. The specimens were randomly assigned to one of the following surface conditioning methods: (1) Hydrofluoric (HF) acid gel (9.5%) etching, (2) Air-borne particle abrasion (50 µm Al\textsubscript{2}O\textsubscript{3}), (3) Silica coating (30 µm SiO\textsubscript{x}, CoJet\textsuperscript{®}-Sand). After each conditioning method, silane coupling agent was applied. Adhesive resin was then applied a thin layer and light polymerized. The low-viscous diacrylate resin composite was bonded to the conditioned substrates using polyethylene molds. All specimens were tested at dry and thermocycled (6.000, 5 °C-55 °C, 30 s) conditions. One-way ANOVA showed significant influence of the surface conditioning methods (p < 0.001), and the PFC types (p < 0.0001) on the shear bond strength values. Significant differences were observed in bond strength values between the acid etched specimens (5.7-14.3 MPa) and those treated with either air-borne particle abrasion (13.0-22.5 MPa) or silica coating (25.5-41.8 MPa) in dry conditions (ANOVA, p < 0.001). After thermocycling, the silica coating process resulted in the highest bond values in all material groups (17.2-30.3 MPa).

Keywords: Air-borne particle abrasion, fracture, hydrofluoric acid, repair, silanization, silica coating

1. Introduction

In today’s dentistry PFC materials, applied directly or indirectly, occupy a paramount position and they achieve acceptable longevity with much lower cost than their ceramic counterparts. PFC restorations, especially when used
as laminates, allow for minimally invasive preparations, or no preparations at all, for the replacement of missing dental tissues by means of basic layering technique.

Novel dental polymers today generally consist of a monomeric matrix resin, silanated inorganic fillers, a polymerization initiator system, inhibitors for storage stability, and pigmentation for shading. Although marked improvements have been noted in terms of physical and mechanical properties during the last 10-20 years, enzymes and alcohol present in the oral cavity, for instance, can degrade the composite matrix [1-3]. Moreover, composites are less stable in fluids and their degradation rate is higher in saliva simulating conditions, depending on the chemical nature of the monomers, amount of dimers and oligomers, the degree of cross-linking in the polymerized matrix, and other intraoral impact [4-6]. In addition, fatigue can accelerate the wear process in composite materials. All these factors provoke discoloration, degradation, microleakage, wear, ditching at the margins, delamination or simply fracture being often experienced in clinical conditions, which in turn, may require repair or replacement of the restoration [7-11].

Repair as an alternative to complete removal, would preserve the tooth as it is often difficult to remove an adhesive restoration without removing an integral part of the tooth or the restoration itself and thereby prolong the service life of such restorations [12, 13].

A number of techniques have been proposed to improve composite repair strengths through roughening, etching the substrate surface with acidulated phosphate fluoride, HF acid gel, air-borne particle abrasion or using adhesive resins [14-21]. While several researchers found that the surface roughness of the composite was an important factor in developing high repair strength [21, 22], others reported that grinding or roughening of the bonding surface decreased the bond strength [15, 20, 23]. Despite the hazardous effects of HF acid gel, etching the surface of a composite restoration with this acid followed by the application of a silane coupling agent is a well-known and recommended method to increase bond strength. Although HF acid was found effective in roughening the composite surface for bonding resin composite [24, 25], neither etching with these solutions nor adding silane resulted in an adequate resin bond to some resin composites [26-29].

Recent developments in surface conditioning methods have resulted in improved resin-to-resin bond strengths. One alternative has been introduced with the use of silica coating and silanization [30]. Although comparative studies showing the advantages of various types of surface conditioning methods on different composites exist, there seems to be no consensus in the literature regarding the best conditioning method for individual PFCs.
Therefore, the objectives of this study were to evaluate the effect of three surface conditioning methods on the shear bond strength of a PFC to five PFC materials and to identify whether there exists an optimum method.

2. Materials and methods

Thirty-six specimens were made from five brands of PFC materials, namely Gradia (GRA), Sculpture (SCU), Sinfony (SIN), Targis (TAR), Tetric Ceram (TET) (total number of specimens=180). The composites were dispensed with a hand instrument into cylindrical (diameter: 6 mm, thickness: 2 mm) undercut cavities prepared in auto-polymerized poly(methylmethacrylate) (Palapress, Vario, Heraeus Kulzer) and polymerized incrementally according to each manufacturers’ recommendations. Table I and II summarize the characteristics of PFC types with codes and manufacturing company names.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Abbreviation</th>
<th>Matrix type</th>
<th>Manufacturer</th>
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<tbody>
<tr>
<td>Gradia</td>
<td>GRA</td>
<td>UEDMA/ethylene dimethacrylate¹</td>
<td>GC, USA</td>
</tr>
<tr>
<td>Sculpture</td>
<td>SCU</td>
<td>dimethacrylate²</td>
<td>Jeneric Pentron, USA</td>
</tr>
<tr>
<td>Sinfony</td>
<td>SIN</td>
<td>HEMA/diacrylate³</td>
<td>3M ESPE, Germany</td>
</tr>
<tr>
<td>Targis</td>
<td>TAR</td>
<td>Bis-GMA, DDMMA, UEDMA, TEGDMA⁴</td>
<td>Ivoclar Vivadent AG, Liechtenstein</td>
</tr>
<tr>
<td>Tetric Ceram</td>
<td>TET</td>
<td>Bis-GMA, UEDMA, TEGDMA⁵</td>
<td>Ivoclar Vivadent AG, Liechtenstein</td>
</tr>
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Bis-GMA = Bis-phenol-A-glycidylmethacrylate
UEDMA = Urethane dimethacrylate
TEGDMA = Triethylene glycol dimethacrylate
DDDMA = Decandiol dimethacrylate
HEMA = 2-hydroxyethyl methacrylate

¹ UDMA (10-25%) and ethylene dimethacrylate (5-10%)
² dimethacrylate
³ 10-30-% (octahydro-4,7-methano-1H-indenediyl) bis(methylene)diacrylate
⁴ Bis-GMA (9%), DDMMA (4.8%), UEDMA (9.3%)
⁵ Bis-GMA (<9%), TEGDMA (<5%), UEDMA (<8%)
TABLE II. Filler types and percentages of particulate filler composites with codes.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Abbreviation</th>
<th>Filler type and content</th>
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<tbody>
<tr>
<td>Gradia</td>
<td>GRA</td>
<td>alumina silicate glass (40-50 w-%), amorphous precipitated silica (5-10 w-%)</td>
</tr>
<tr>
<td>Sculpture</td>
<td>SCU</td>
<td>glass-infiltrated alumina (70 w-%)</td>
</tr>
<tr>
<td>Sinfony</td>
<td>SIN</td>
<td>strontium-aluminium borosilicate glass, silicon oxide (50 w-%)</td>
</tr>
<tr>
<td>Targis</td>
<td>TAR</td>
<td>silanized barium glass fillers (46.2 w-%), highly dispersed silica (11.8 w-%), mixed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxides (18.2 w-%), catalyst and stabilizers (0.8 w-%), pigments (≤0.1 w-%)</td>
</tr>
<tr>
<td>Tetric Ceram</td>
<td>TET</td>
<td>Silanated Ba-glass, ytterbium trifluoride, silanated metal oxide, silanated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>barium-aluminum-fluoro-silicate glass, silanated silica glass (79 w-%)</td>
</tr>
</tbody>
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The exposed surface of each specimen was ground finished to 1200 grit silicon carbide abrasive (Struers RotoPol 11, Struers A/S) and cleaned for 10 min in an ultrasonic bath (Quantrex 90 WT, L&R Manufacturing Inc.) containing distilled water and air-dried. Subsequently, the substrates in each PFC group (n=6) were randomly assigned to each of the following three conditioning methods:

2.1 Surface conditioning methods

Method 1: The substrates were etched with 9.5% HF acid gel (Ultradent® Porcelain Etch) for 90 s in accordance with the manufacturer’s recommendations.

Method 2: Air-borne particle abrasion with 50 µm Al₂O₃ (Korox®, Bego) was applied using an intraoral air abrasion device (Dento-PrepTM, RØNVIG A/S) from a distance of approximately 10 mm at a pressure of 2.5 bars for 4 s.

Method 3 was based on silica coating process that was achieved using the same device under the same conditions but this time it was filled with 30 µm SiOₓ (CoJet®-Sand, 3M ESPE AG).

The conditioned substrates were then coated with a 3-methacyloyxpropyltrimethoxysilane coupling agent, γ-MPS (ESPE®-Sil, 3M ESPE AG) and waited for its reaction for 5 min. Intermediate monomer resin (IMR) (Scotchbond Multipurpose Adhesive, 3M Dental Products) was applied a thin layer and it was light-polymerized (Optilux 501, Kerr) for 10 s.

In an additional experiment, (n=15, 1/group) the conditioned surfaces of the five substrates were first gold sputtered and then examined using a scanning electron microscopy, SEM, (JSM-5500, Jeol Instruments).
2.2 Bonding procedures

The bonding procedures were carried out in accordance with the manufacturers’ instructions by the same operator (M.Ö.) throughout the experiments. The low-viscous diacrylate resin composite (Sinfony Dentin, Shade A2, 3M ESPE) was bonded onto the conditioned PFC substrates using translucent polyethylene molds with inner diameter of 3.6 mm and height of 5 mm. The resin composite was packed against the substrate with a composite-filling instrument and polymerized in a light-curing oven (Visio Beta Vario, 3M ESPE) for 40 s. Polyethylene molds were gently removed from the test specimens.

All groups of PFC/conditioning method combinations were randomly divided into 2 groups (n=6) for dry and thermocycled storing conditions. While dry samples were kept in a dessicator at room temperature for 24 h prior to testing, the other groups were subjected to thermocycling (Thermocycler 2000, Heto-Holten A/S) for 6,000 cycles between 5 ºC and 55 ºC in deionised grade 3 water. The dwelling time at each temperature was 30 s. The transfer time from one bath to the other was 2 s.

Specimens were mounted in a jig (Bencor Multi-T shear assembly, Danville Engineering Inc.) of the universal testing machine (Lloyd LRX, Lloyd Instruments Ltd) and the shear force was applied to the adhesive interface until failure occurred. The specimens were loaded at a crosshead speed of 1.0 mm/min and the stress-strain curve was analyzed with Nexygen 2.0 software (Lloyd LRX, Lloyd Instruments Ltd).

Statistical analysis was performed using SAS System for Windows, release 8.02/2001 (SAS Institute Inc). P values less than 0.05 were considered to be statistically significant in all tests. The differences in means of each group were analysed by analysis of variance (ANOVA) with shear bond strength as the dependent variable, the surface conditioning methods and the PFC types as the independent factors. Since the interaction between surface conditioning methods and PFC types were statistically significant (two-way ANOVA, p < 0.0001) in dry and thermocycled conditions, one-way ANOVA with multiple comparisons using Tukey-Kramer adjustment test was used for further analyses. Furthermore, two-sample t-test was used to determine the significant differences between dry and thermocycled conditions.

3. Results

The results of the shear bond strength test for HF acid etching, airborne
particle abrasion and silica coating are presented in Figs. 1a-c. One-way analysis of variance (ANOVA) showed significant influence of the surface conditioning methods \((p < 0.0001)\), and PFC type on the bond strength values \((p < 0.001)\). The differences in bond strength between storage conditions were significant except for TAR after air-borne particle abrasion \((\text{two-sample t-test}, p < 0.05)\).

![Acid etching](image)

**Fig. 1a**

![Air particle abrasion](image)

**Fig. 1b**

![Silica coating](image)

**Fig. 1c**

*Fig. 1 a-c. Shear bond strengths after a) Hydrofluoric acid etching, b) Air-borne particle abrasion and c) Silica coating at dry and thermocycled conditions. Vertical lines represent the standard deviations. For abbreviations, see Table I.*
Conditioning the PFC substrates with the HF acid etching resulted in the least favourable bond strength values amongst all conditioning methods ranging between 5.7 MPa and 14.3 MPa in dry conditions and between 3.3 MPa and 9.5 MPa after thermocycling. In dry conditions after HF acid etching, there were significant differences between SIN vs TET (p = 0.047), TAR vs TET (p = 0.002). After thermocycling, there were significant differences between SIN vs TAR (p = 0.0007), SIN vs TET (p = 0.0002) in the HF acid etched groups.

In the air particle treated group, bond strengths increased significantly compared to HF acid etching for GRA (13.0 MPa, p = 0.0007), SCU (15.7 MPa, p = 0.0001), SIN (22.5 MPa, p = 0.0001), TAR (20.0 MPa, p = 0.02) and TET (14.8 MPa, p = 0.0009) in dry conditions and for SIN (18.0 MPa, p = 0.01), TAR (21.2 MPa, p < 0.0001) and TET (12.5 MPa, p < 0.0001 MPa) after thermocycling.

Significantly higher (p < 0.0001), bond strengths were achieved after silica coating and silanization amongst all the conditioning methods for all types of PFCs ranging between 25.5 MPa and 41.8 MPa except for TAR after air-borne particle abrasion vs silica coating (p = 0.17) in dry conditions.

SEM analysis, complementary to the shear bond strength tests, revealed that HF acid gel dissolves the filler components of the PFCs and produces porous irregular surfaces (Fig. 2a-e). On the other hand, airborne particle treated groups either with Al2O3 or SiOx exhibited similar rough surfaces covered with abundant sand particles on the substrate surfaces (Fig. 3a-b).
Fig. 2 a-e. Typical SEM view of a) GRA, b) SCU, c) SIN, d) TAR, e) TET PFC substrates exposed to 9.5% HF acid gel application for 90 s and rinsing. Note that the acid treatment dissolved the filler components of the substrates (original magnification x 5000).

Fig. 3 a-b. Typical SEM view of a) GRA and b) TET after airborne particle abrasion with alumina and SiO_{2}, respectively. Note that the surfaces were covered with abundant sand particles (original magnification x 5000).
4. Discussion

The results of this study indicated that conditioning the substrates with HF acid gel adversely affected the morphological features of PFC substrates thereby resulting in poor repair strength when compared with other methods tested.

Usually inorganic fillers are integrated into the polymer matrix by silane coupling agents, that form an interface between hydrophobic resin matrix and hydrophilic filler particles. In most situations, hydrolyzed γ-MPS is used as a coupling agent for the fillers. Fluoride ion is implicated in depolymerization reactions of matrix-filler interface. When PFC substrates are exposed to HF acid gel, water monolayer may penetrate via voids to fillers, that in turn, may disorganize the siloxane network formed from the condensation of intermolecular silanol groups, which is responsible for stabilizing the filler-resin interface [31]. All these mechanisms may weaken the particle-matrix interface that leads to filler dissolution. This phenomenon was evidently observed in the SEM analysis where a great portion of the fillers were detached from the matrix after they were exposed to HF acid etching.

One important aspect of filler erosion after HF acid gel treatment is dependent on the filler type. It has been reported that barium, boroaluminosilicate, silicate, strontium glass, and zinc glasses exhibited extended degradation on acid attack, whereas quartz, silica, lithium aluminosilicates and their mixtures showed less involvement [32, 33]. The SEM findings revealed that more fillers were dissolved in highly filled TET (79 w-%) that is composed of silica and barium fillers. A high filler content adversely affects processing and on the other hand, too much cross-linking of the resins could embrittle the material that was observed with TET. The morphologic and compositional changes in patterns obtained for the materials after etching are also dependent on the type of acid used as well as the composition of the restorative material. Although fluorides with lower concentrations like 1.23% APF were used, similar findings were reported in some previous studies where APF was found to dissolve the fillers and caused degradation [34]. Nevertheless, etching the PFCs with a 9.5% HF gel for 90 s resulted in variations in repair strength dependent on the composite material. This is in line with the study of Swift et al [24] where they found that etching with 9.5% HF acid gel for 30 s either increased or decreased the repair strengths of composites. This finding together with ours could be explained on the grounds of variations in matrix composition. All the monomers used in current composite techniques are organic esters of methyl methacrylate derivatives. Generally, organic esters in low pH undergo hydrolytic cleavage of the ester group.
Increased filler dissolution after HF acid conditioning might result in increased surface area exposure of the resin matrix and consequently an accelerated hydrolytic effect. This phenomenon was very evident in high filled PFCs with similar filler types (TAR, TET) when compared to a relatively low filled one (SIN).

Bond strength is dependent on unconverted C=C double bonds on the resin, which may be attributed to either a low conversion rate or a high matrix portion. The bond between the substrate and new resin is also based on unreacted C=C double bonds of the functional groups on the surface of polymer matrix. A high degree of conversion that resulted from the use of heat and light used for polymerization causes improvement in mechanical strength and hardness and therefore makes the attachment of the new composite more difficult. Controversy still exists regarding whether the degree of conversion is compromised when PFCs are photo-activated [33]. However, it was also assumed that a certain percentage of unconverted C=C double bonds are available even after laboratory processing [35]. In this study, in dry conditions satisfactory bond strengths were obtained according to ISO standards [36]. Although the substrates were only ground finished, there might be some unreacted carbon bonds available on the surface. However to what extent those types of unreacted bonding sites existed in the PFC materials, needs further clarification, namely using e.g. infrared spectroscopy for the surface characterization.

In FTIR (Fourier transformation infrared spectroscopic) evaluations that has been already published, it was found that the UEDMA/TEGDMA phase had a conversion rate of 70% and exhibited superior wear resistance, while the Bis-GMA/TEGDMA had a conversion rate of 55% [37]. The least favourable results obtained with GRA could be attributed to its high UEDMA matrix content. In PFCs with such matrix content, the possibility to obtain free radical polymerization bonding is low because of relatively small number of unreacted C=C double bonds on the polymer surface [38]. Monomer mixtures of Bis-GMA and TEGDMA give rise to polymers in which the quantity of remaining double bonds increases with the content of Bis-GMA, without the mechanical properties being significantly effected [39].

An interesting result was achieved with the SIN composite, with octahydro-4,7-mathano-1H-indenediyl)bis(methylene)-diacrylate, in its monomer matrix. It showed high bond strengths, similar to those of Bis-GMA/TEGDMA PFCs, with also less decrease after thermocycling. One reason for this may be related to the function of IMR that may bond covalently to the pendant, unreacted methacrylate groups. It has been reported earlier that swelling of the composite substrate surface with different solvents and the use of low-viscosity IMR
influence the bond between two composites [20, 38, 40]. The functions of IMR are to achieve better wetting of the substrate surface and to some degree dissolve and swell the polymer surface of the substrate. The hydrophilic adhesive joint in GRA, SCU, TAR, TET may be less rigid than the adhesive joint made by hydrophobic monomer resin such as the main monomer of SIN.

After air-particle abrasion, either with Al$_2$O$_3$ or SiO$_x$ followed by silanization, significant increase in bond strengths was noted. When comparing the results of the acid etched groups with those of air-abraded ones, the function of silane coupling agent should not be disregarded. In this study, $\gamma$-MPS was chosen because of the compatibility of the methacrylate moiety for copolymerization with the PFC. Silane treatment also improves the wettability of the filler, affects its surface energy, hence its dispersion in the matrix. However when little or no filler remains after HF conditioning, this effect of silane could obviously not profited from. One can anticipate that alumina or silica on the surface of the substrate could form strong enough chemical bonds, covalent bridges, through its surface hydroxyl groups with hydrolyzed silanol groups of the silane:-Al-O-Si- or –Si-O-Si. The methacrylate groups of the organosilane $\gamma$-MPS compound form covalent bonds with the resin when polymerized.

It is difficult to compare our results with previous studies as storage conditions are not the same but our findings after thermocycling with the use of air-particle abrasion with either alumina or silica followed by silane coupling agent and IMR application were higher than those reports where specimens were tested either after short term water storage [34] or lower number of thermocycles [28]. After thermocycling, the bond strengths provided were well above the recommended ISO standards [36]. While some studies reported that the type and chemical structure of repair resin have no influence on the strength of the repair [35], some others proved that the use of silica coating provided a significant improvement in the repair strength [28, 30]. Boyer et al [40] found that highly filled resin composites provided higher bond strengths which contradicts with our findings and warrants further research.

Water uptake has an important role in the chemical degradation of composite materials that mainly takes place in the resin matrix that is a diffusion controlled process with the diffusion coefficient decreasing with the concentration of water in the matrix. Many resin composite bonding studies have addressed the effect of storage time in water on bond strength of repairs. Söderholm and Roberts [41] found that the repair resin had a tendency to weaken when they were stored in water for 3 and 12 months. The variation in coefficient of thermal expansion of materials and especially intermediate resin could be factors responsible for the reduction of bond strength after thermocycling.
In clinical situations, when PFC substrates need to be conditioned prior to bonding new resin, factors such as age of the substrate, surface chemistry and morphology play role on the bond strength due to degradation in the oral environment. Of course they affect the adhesion and require further investigations.

5. Conclusions

Within the limitations of this study, the following conclusions were made:
1. Composite-to-composite adhesion strengths varied in accordance with the PFC types and surface conditioning methods tested.
2. HF acid gel dissolved the filler particles but resulted in lower bond strengths than alumina particle abrasion and silica coating.
3. Air-particle abrasion with silica particles followed by silanization increased the bond strengths regardless of the PFC type.
4. When compared to dry testing conditions, bond strengths decreased after thermocycling in all HF acid gel treated substrates but no significant change was noted after alumina particle abrasion or silica coating followed by silanization.

References