ALL CERAMIC CEMENTATION: A KEY TO SUCCESSFUL RESTORATION

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ABSTRACT: All-ceramic restorations are considered no more as future but established and scientifically documented reality of our daily activities as dental practitioner. To ensure successful and long-term durability of all ceramic restorations, one of the key requirements is adequate cementation. In spite of using all ceramic restorations so frequently in our routine practice, very few are aware of exact bonding mechanism for it. This review enlightens us about all the aspects of all ceramic cementation.

KEYWORDS: All-ceramic, restorations, bonding, cementation, Adhesion, etching, sandblasting.

INTRODUCTION

The longevity and success of indirect restorations are influenced by patient and operator. The patient manages oral hygiene, diet and functional habits while the operator manages tooth preparation, impression and cementation. Cementation is a crucial step in the process of ensuring the retention, marginal seal and durability of indirect restorations. To achieve a successful outcome, the clinician must understand the ceramic type, surface treatment, cement to be used and procedure, because the ceramic surface treatment before cementation varies according to the type of ceramic used 1.

Types of Ceramics

Dental ceramic systems can be classified according to their matrix material, filler and dopant. Three main categories of dental ceramics have been described in the literature 2,3:
- Predominantly glass
- Particle-filled glass and
- Polycrystalline (non-glass) ceramics.

Predominantly Glass

It is also known as feldspathic ceramics. This ceramic is highly esthetic, biocompatible, and resistant to abrasion and compressive forces. It is used as a veneering material over metal or ceramic copings, inlays, onlays and porcelain veneers (CEREC Blocks; Sirona Dental System, Ceramco 3; Dentsply, York, Pa.). It also is characterized by low mechanical strength in comparison with other ceramic types and must be cemented to the prepared tooth adhesively so as to increase the restoration’s resistance to fracture 1.

Particle-filled Glass

These types of ceramics consist of various amounts and types of particles and a glassy matrix. They are of mainly three types:
- Leucite reinforced (Low-filled)
- Lithium disilicate reinforced (Intermediate filled)
- Glass infiltrated aluminum oxide ceramics

Leucite reinforced (Low-filled)

Leucite-reinforced ceramics contain up to 45% by volume of leucite which acts as crack deflectors and contribute to increased resistance to crack propagation. They are indicated in esthetic veneers, anterior crowns, as layering porcelain on leucite-reinforced, lithium disilicate, alumina, or zirconia cores (IPS Empress Esthetic; Ivoclar Vivadent and OPC; Jeneric Pentron, Wallingford, Conn.). These ceramics need to be cemented adhesively to improve their strength 1,4,5.

Lithium disilicate reinforced (Intermediate filled)

Lithium disilicate ceramics consist of about 65% by volume of highly interlocking lithium disilicate crystals dispersed in a glassy matrix. They are indicated in Veneers, inlays, onlays, crowns and three-unit bridges – anterior and premolar region (IPS e.max Press; Ivoclar Vivadent and OPC 3G; Jeneric Pentron). This material can be cemented adhesively or nonadhesively when used with...
full-coverage restorations; clinical studies have reported no difference between the two types of cementation.\(^5,6,7\)

**Glass infiltrated aluminium oxide ceramics**

This category includes In-Ceram Alumina, In-Ceram Spinell and In-Ceram Zirconia (Vita Zahnfabrik). In-Ceram Spinell is indicated in anterior crowns, anterior inlays, onlays and veneers; In-Ceram Alumina is indicated in anterior and posterior crowns, anterior FPD’s and In-Ceram Zirconia is indicated in posterior crowns and posterior FPD’s. They are cemented conventionally rather than adhesively, because etching glass with HF acid does not appear to increase the retention of resin cements. Some researchers have reported that coating the ceramic with tribochemical silica and air abrading the intaglio surface, followed by the application of 10-methacryloxyloxyethyl dihydrogen phosphate (MDP) (a silane and phosphate monomer) before using resin cement, improves the bond to this type of ceramic.\(^5,8,9,10\)

**Polycrystalline (non-glass) ceramics**

Polycrystalline ceramics are densely sintered aluminum oxide or zirconium oxide and are characterized by the absence of glass in their composition. These ceramics possess high toughness and strength. Zirconia is of particular interest because of its transformation toughening and colour masking properties due to its dense crystalline structure (Procera Alumina; Nobel Biocare, Zurich, Cercon Zirconia; Dentsply, Lava Zirconia; 3M ESPE, St. Paul, Minn., IPS e.max ZirCAD; Ivoclar Vivadent). They are indicated in anterior and posterior crowns, bruxers – full-contour crowns, anterior and posterior bridges (maximum 14-unit bridges, span depends on product and number of abutments, endodontically treated teeth, implant abutments, inlay bridges, maryland bridges and block-out of darkened tooth structure or cores. Polycrystalline ceramics most often are cemented conventionally but, in certain circumstances, adhesive cementation can be done. Use of air abrasion with 50-micrometer aluminum oxide powder at 7.0 pounds per square inch followed by application of a primer containing MDP before application of the resin cement has been recommended in instances where increased retention is required.\(^5\)

**Adhesive System**

Adhesion or bonding is the process of forming an adhesive joint, which consists of two substrates joined together. Dental adhesives are solutions of resin monomers that join a restorative material with a dental substrate after the monomers set by polymerization. The success of adhesive bonding relies on mechanical bonding through micromechanical interlocking from surface roughening and chemical bonding between ceramic and cement.\(^11\)

**Bonding to enamel and dentin**

Dental adhesive joints may be more complex such as the enamel–adhesive–composite– adhesive–porcelain interface formed when a clinician bonds a porcelain restoration (Fig.1).

In 1955, Buonocore\(^12\) reported the use of 85% phosphoric acid to improve the retention of an acrylic resin on enamel. The micromechanical nature of the interaction of dental adhesives with enamel is a result of the infiltration of resin monomers into the microporosities left by the acid dissolution of enamel and subsequent enveloping of the exposed hydroxyapatite crystals with the polymerized monomers within the pores on the enamel surface.\(^13\) This task is difficult to achieve as the bonding process for enamel is different from that for dentin. That is, dentin is more humid and more organic than enamel. While enamel is composed of 96% hydroxyapatite (mineral) by weight, dentin contains a significant amount of water and organic material, mainly type-I collagen.\(^15\) This humid and organic nature of dentin makes bonding to this hard tissue extremely difficult.

The age of the patient also plays a significant role, because dentin undergoes age-associated changes i.e., young dentin has wide and open tubules, but the older a patient is, the lower the number of open tubules and the smaller their diameters due to the composition of secondary and tertiary dentin (sclerotic process). Complete occlusion of the tubules occurs and prevents the desired tag formation of the composite cements. This leads to further reduced bond strength, because the penetration of resin into and via the dentinal tubules is responsible for nearly 40% of that strength.\(^15\)

When tooth structure is cut with a bur or other instrument, the residual components form a “smear layer” of debris on the surface.\(^17\) This debris forms a uniform coating on enamel and dentin and plugs the entrance of the dentinal tubules, reducing the permeability of dentin. The smear layer is porous and permeable as a result of submicron channels that allow the dentinal fluid to pass through.\(^14\) The basic composition of the smear layer is hydroxyapatite and altered collagen with an external surface formed by gel-like denatured collagen.\(^18\) As the smear layer constitutes a true physical barrier, it must be dissolved or made permeable so the monomers in the adhesives can contact the dentin surface directly. In spite of different classifications of adhesive systems, the current adhesion strategies depend exclusively on how dental adhesives interact with this smear layer. One strategy involves etch-and-rinse (total etch) adhesives, which remove the smear layer and superficial hydroxyapatite.
through etching with a separate acid gel. The second strategy involves self-etch adhesives, which make the smear layer permeable without removing it completely\(^{11}\).

**Etch-and-rinse strategy (Total etch)**

In this strategy, dentin and enamel are treated with an acid gel (commonly phosphoric acid) to remove the smear layer and demineralized the most superficial hydroxyapatite crystals. Following this chemical etching, a mixture of resin monomers (primer/adhesive) dissolved in an organic solvent is applied to infiltrate etched dentin\(^ {19}\). The resin monomers permeate the water-filled spaces between adjacent dentin collagen fibers that used to be occupied by hydroxyapatite crystals. This infiltration results in a hybrid tissue composed of collagen, resin, residual hydroxyapatite, and traces of water (Fig. 2) known as the resin–dentin interdiffusion zone, first described in 1982 as the hybrid layer\(^ {20}\). This intimate micromechanical entanglement of resin monomers with etched dentin may result in decreased postoperative sensitivity, may make for a better marginal fit, and may even act as an elastic buffer that compensates for the polymerization shrinkage stress during contraction of the restorative composite\(^ {11}\).

**Self-etch (non-rinsing) strategy**

These adhesives do not require a separate acid-etch step as they condition and prime enamel and dentin simultaneously by infiltrating and partially dissolving the smear layer and hydroxyapatite to generate a hybrid zone that incorporates minerals and the smear layer\(^ {11}\). The first self-etch nonrinsing adhesives were composed of two solutions; an acidic primer and a bonding resin (Fig. 3). Recently, many clinicians have shifted to one-step self-etch systems (also named all-in-one adhesives) in which manufacturers have attempted to incorporate all the primary components of an adhesive system (etchant, primer, and bonding resin) into a single solution (Fig. 4). All-in-one adhesives are user-friendly in that fewer steps are required for the bonding protocol. The elimination of separate etching and rinsing steps simplified the bonding technique, making these systems more popular in daily practice\(^ {21}\). Self-etch adhesives differ in their aggressiveness. Therefore they are classified in three categories according to acidity: mild, moderate, and aggressive\(^ {22}\).

**Enamel bonding with self-etch adhesives**

The enamel bond strengths of the earliest self-etch adhesives were lower than those associated with adhesives that rely on a separate etching step. Because of their higher pH, two-step self-etch adhesives result in shallower enamel demineralization compared with that of phosphoric acid. Nevertheless, roughening of enamel to remove prismless enamel improves the enamel-bonding ability of self-etch adhesives\(^ {11}\). All-in-one self-etch systems are not as acidic as the phosphoric acid used with the etch-and-rinse adhesives\(^ {15}\). This characteristic has raised concerns about the performance of all-in-one self-etch systems on intact enamel. Several in vitro investigations have reported lower resin–enamel bond strength of all-in-one self-etch materials\(^ {23,24,25}\). Grinding the enamel during a bevel or cavity preparation, for
instance, makes the substrate more receptive for bonding with all-in-one self-etch systems. Despite the increased popularity of self-etch adhesives, etching with phosphoric acid is still considered the golden standard against which new materials are tested.

**Dentin bonding with self-etch adhesives**

In spite of their low technique sensitivity and user-friendliness, all-in-one adhesives have resulted in low bonding effectiveness in vitro while their clinical reliability has often been questioned. Another drawback associated with all-in-one adhesives is their behavior as semi-permeable membranes. These materials allow the movement of water across the bonded interface, which potentially leads to hydrolytic degradation.

Because of the high hydrophilic nature of the acidic monomers and the high water concentration required for ionization of the acidic monomers in all-in-one self-etch solutions, these materials are likely to have resin–enamel bonds compromised over time. An inadequate resin penetration into tooth substrates may result in accelerated degradation of the structure of the bonding interface. As polymerization shrinkage stresses the bonding interface, dentin adhesives that do not resist these stresses result in low bond strengths, marginal gaps, recurrent caries, and pulpal irritation.

The magnitude of dentin bond strengths depends on the degree of infiltration of the resin monomers into the collagen pretreated with an acidic conditioner or with phosphoric acid. The author’s electron microscopy analyses have demonstrated that acetone-based all-in-one adhesives result in a hybrid layer 0.2 to 0.5 mm thick, interfacial gaps, and limited resin penetration into the dentinal tubules.

Other factors include Porosities (or blisters) occur at the enamel and dentin bonding interfaces because most all-in-one adhesives behave as semi-permeable membranes. These porosities may be a result of water accumulation either caused by an osmotic gradient or by monomer–solvent phase separation upon evaporation of the acetone. The number and size of these blisters may also depend on the intensity of the air-drying step.

**Methods of mechanical bonding for ceramic restorations**

**Hydrofluoric acid etching**

It is considered to be one of the most common surface treatment methods for adhesive cementation to ceramic restorations. Phosphoric acid (H₃PO₄) or hydrofluoric acids (HF) etching are commonly recommended methods used to surface roughen silica-based ceramics (Glass filled and Particle filled). HF removes the glassy matrix of glass ceramics creating a high surface energy substrate with microporosities for the penetration and polymerization of resin composites, that is, enabling a micromechanical interlocking. However, HF etching does not produce any change in arithmetic roughness (Ra) of ZrO₂. The lack of silica also removes the chemical bonding between silica–silane necessary for silanization. The negligible effect of the HF on the ZrO₂ surface occurs due to the absence of glassy matrix, resulting in low bond strength values.

### Table 1. Summary of surface treatment procedures for different types of ceramics.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Filler</th>
<th>Surface Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predominantly Glass</td>
<td>Aluminum oxide</td>
<td>Apply 10 percent hydrofluoric (HF) acid for 1 minute, rinse and dry; apply silane for 1 minute, air dry</td>
</tr>
<tr>
<td>Particle-Filled Glass</td>
<td>Leucite</td>
<td>Apply 5 percent HF acid for 1 minute, rinse and dry; apply silane for 1 minute, air dry</td>
</tr>
<tr>
<td></td>
<td>Lithium disilicate</td>
<td>Apply 5 percent HF acid for 20 seconds, rinse and dry; apply silane for 1 minute, air dry</td>
</tr>
<tr>
<td></td>
<td>Glass-infiltrated alumina</td>
<td>Perform air abrasion with tribochemical silica coating or aluminum oxide; apply an adhesion-promoting agent containing MDP and dry</td>
</tr>
<tr>
<td>Polycrystalline</td>
<td>Aluminum oxide</td>
<td>Perform air abrasion with aluminum oxide; apply an adhesion-promoting agent containing MDP and dry</td>
</tr>
<tr>
<td></td>
<td>Zirconium oxide</td>
<td>Air abrasion with 50-micrometer aluminum oxide powder at 7 pounds per square inch; apply an adhesion-promoting agent containing MDP and dry</td>
</tr>
</tbody>
</table>

* MDP: 10-methacryloyloxydecyl dihydrogen phosphate
Surface grinding

Surface grinding is a commonly used alternative for roughening the surface of ZrO₂ to improve mechanical bonding. There are several methods used for surface grinding like grinding using abrasive paper or wheels (SiC or Al₂O₃) or particle air-abrasion using Al₂O₃ or other abrasive particles ranging in size from 50 to 250 micrometer. However, research has shown that surface grinding techniques, using traditional resin cements, have no significant effect on increasing the bond strength of zirconia to resin cements. Another problem with these techniques is that they can create surface microcracks. These flaws act as crack initiation sites that can decrease strength and apparent fracture toughness.

Sandblasting

Guazzato et al and Kosmac et al showed that sandblasting produced the most effective tetragonal to monoclinic phase change when compared to fine polishing, grinding with an abrasive wheel, or grinding using a diamond bur. Sandblasting is able to induce transformation at low temperature, with minimal surface damage.

Fused glass micro pearls

Slurry of micropearls was painted on a ZrO₂ surface and fired in a furnace. The fused glass film increased surface roughness of ZrO₂, allowing increased micro-retention. The silica-rich film also allows for silanization of ZrO₂ before bonding, making it possible to form siloxane bonds to resin cement. Derand et al. showed that use of this fused micro-pearl film significantly increased the bond strength of ZrO₂ (11.3–18.4MPa) compared to untreated or silanized ZrO₂ (0.5–1.5MPa).

Selective infiltration etching [SIE]

A novel surface roughening technique that has been explored for ZrO₂ is selective infiltration etching. SIE uses heat-induced maturation process to pre-stress surface grain boundaries in ZrO₂ to allow infiltration of boundaries with molten glass. The glass is then etched out using HF, creating a 3D network of inter-granular porosity that allows nano-mechanical interlocking of resin cement. The advantage of SIE is that it only involves grains that are exposed to molten glass, allowing control of the area to be etched. Aboushelib et al showed that using SIE on ZrO₂ resulted in increased microtensile bond strength (49.8±2.7MPa) when compared to particle air-abraded ZrO₂ (33.4±2.1MPa). The use of SIE improved nano-mechanical retention of zirconia by increasing the surface area available for bonding.

Hot chemical etching

The use of a hot chemical etching solution has been proposed to etch the wings of Maryland bridges. Application of hot chemical etching solution produces a surface roughness that is significantly greater than SIE.
Chemical bonding
Silane coupling agent

Organo-silanes, generally referred to as "silanes" in dentistry, are compounds that contain a silicon (Si) atom or atoms which are similar to orthoesters in structure, and display dual reactivity. One end of a silane molecule is organically functional (e.g., vinyl–CH2=CH2, amino–NH2), and can polymerize with an organic matrix (e.g., a methacrylate). The other end is generally comprised of alkoxy groups (e.g., methoxy–OCH3, ethoxy–OCH2CH3), which can react with a hydroxylated surface, like porcelain\(^30\) (Fig. 4). Silanes are also believed to promote surface wetting, which enhances potential micromechanical retention with low viscosity resin cements\(^{37,38}\). Traditional silane chemistry is not truly effective with ZrO\(_2\), as it possesses a relatively non-polar surface, is more chemically stable than silica-containing ceramics, and not easily hydrolyzed\(^{30}\).

Hydrolyzed and unhydrolyzed silanes are available. Hydrolyzed silanes most commonly are one-bottle systems with a short shelf life; if used after expiration date, can be detrimental to the bond. Unhydrolyzed or "inactive" silanes are two-bottle systems that the clinician mixes before application to ensure a fresh and active silane and a longer shelf life than that of dual polymerized resin cements\(^1\).

Tribochemical silica coating

Tribochemical silica coating with impact energy of blasted silicate particles produces bonding between the silicate and the targeted surface by mechano-chemical reaction. Application of a tribochemical coating, before silanization, significantly enhances bond strength between a treated substrate and resin cement. Cleaning of a tribochemical coated ZrO\(_2\) before resin bonding can be deleterious to bond strength\(^{30}\). (Fig. 5)

Nishigawa et al\(^{39}\) determined that ultrasonic cleaning of tribochemical coated ZrO\(_2\) before silanization and resin bonding significantly decreases bond strength. Cleaning for 2 or 5 min resulted in bond strength statistically similar to air-abrading alone before bonding. Ultrasonic cleaning results in decreased silica content on the surface. This decrease, along surface morphology changes, is thought to cause the loss of bond strength. Air pressure has also been shown to affect bond strength when applying a tribochemical coating. Increasing pressure increases the amount of silica on the ZrO\(_2\) surface. It is thought that increasing air pressure, which increases kinetic energy of particles, causes an increase in surface roughness and the number of particles that contact the surface. This increases mechanical retention the amount of silica available for chemical bonding.

Fig. 3. Interaction of two-bottle self-etch adhesives with dentin.
Silicoating

Applying a silica layer to ZrO₂-based ceramics is silicoating. Silicoating involves pyrolytically applying a silica coating on a substrate surface, followed by application of silane, before bonding using resin cement. Using a lab device, butane gas is burned with atmospheric oxygen and guided over a container filled with tetraethoxy silane. The gas is lit and the silane decomposes in the flame, coating the material with a layer of SiOₓ–C fragments that bond adhesively to the surface of the material.¹⁰

Plasma spray coating

Another form of silicoating uses a plasma spray technique to deposit a siloxane coating on ZrO₂. Derand et al. used a high-frequency generator to deposit hexamethyldisiloxane (HMDS) on the surface of ZrO₂. When polymerized, HMDS acts like a silane, resulting in a siloxane bond between ZrO₂ and resin cement. The application of the plasma produced a bond strength that was significantly greater than untreated or silanized ZrO₂ but was significantly less than ZrO₂ coated with a film of porcelain microparticles.

Vapour phase deposition

Application of a unique vapor-phase deposition technique, in which a chloro-silane gas (SiCl₄) is combined with water vapour to form a SiOₓY functionalized surface on a ZrO₂ substrate. The process uses molecular vapor deposition (MVD), an enhancement on conventional vapor deposition, to deposit ultra-thin, uniform coatings on substrates using an in-situ surface plasma treatment. Piascik et al. showed that ZrO₂ coated with a SiOₓY film, followed by silanization and resin cement bonding, enhanced bond strength. Zirconia with a film thickness of 2.6nm had significantly greater bond strength than tribochemical-coated ZrO₂ and was comparable to porcelain. The ZrO₂ that was bonded using a 23nm SiOₓY film had a significantly lower bond strength than the 2.6nm film coated ZrO₂ but greater than untreated ZrO₂.²⁴

Based on these results, Piascik et al. stated that it is possible that bond strength of the SiOₓY film is dependent on film thickness and decrease in bond strength could be caused by a lack of chemisorption in the additional layers deposited on the ZrO₂ surface after the initial deposited layer.²⁴

Primers

Primers improve bonding between resin cements and various restorative materials and can be classified based on the substrate (silica-based ceramics, alumina, zirconia, alloy) for which they are intended to be used. Silane Primer (silane coupling agent) is based on silane used with silica-based ceramics (feldspathic porcelain, leucite-reinforced ceramic, lithium disilicate ceramic). Ceramic Primer is based on an acidic adhesive monomers used with alumina- and zirconia-based ceramics. Ceramic primers may contain silane and metal primers. 10-methacryloyloxydecyl dihydrogen phosphate or MDP-containing resin cement continues to be the popular choice for luting ZrO₂ prosthetics in clinical applications due to their low incident of failure and loss of retention. Acidic monomers rapidly hydrolyze silane coupling agents, producing the siloxane bonds necessary for chemical bonding. Acidic nature of MDP enhances the polysiloxane bonding produced by silane coupling agents and results in improved retention of resin cements to ZrO₂.²⁵

CONCLUSION

The increasing demand for esthetically pleasing restorations has resulted in the development and introduction of newer dental ceramics. The dentist must select not only the appropriate ceramic, on the basis of functional and esthetic demands, but also the cement and the cementation procedure for each type of ceramic and clinical situation. For the successful outcome, clinician should give special consideration to the use of adhesives, resin cements and field isolation and adhere strictly to manufacturers’ instructions.

Fig 4. Idealized illustration of how silane compounds chemically bond to inorganic silica (left side of figure) and to a polymerizing organic matrix (right side of figure – the double bond circled in red would be broken during a free radical driven polymerization process, facilitating covalent bonding with the polymerizing organic matrix).
Fig. 5. Illustration of the tribochemical silica coating process. Silica coated alumina particles are driven into the ceramic surface under high air pressure. This creates local energy which facilitates transfer of silica onto the ceramic surface. A potential problem is the creation of damage to the surface of the ceramic via the air abrasion process, which could accelerate fatigue.

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