Cements and Adhesives for All-Ceramic Restorations

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Dental luting cements are designed to retain restorations, appliances, and post and cores in a stable and, presumably, long-lasting position in the oral environment. Retention mechanisms are reported to be chemical, mechanical (friction), and micro-mechanical (hybridized tissue), but they are usually a combination of two or three mechanisms, depending on the nature of the cement and of the substrate. Among dental luting cements commercially available, there are resin-based and nonresin-based cements. They must have for their acceptable clinical performance adequate resistance to dissolution, strong bond through mechanical interlocking and adhesion, high strength under tension, good manipulation properties, and also be biologically compatible with the substrate.\textsuperscript{1,2}

Traditionally, zinc phosphate cement has been regarded as the most popular material, despite its disadvantages as low hardness, solubility and lack of adhesion.\textsuperscript{3}

This work was partially supported by Cap grants # 300305/0-4, Brazil, and FAPESP # 04/1263-0, and # 2010/06152-9 Brazil.

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Although the final marginal accuracy of all-ceramic systems processes (computer-aided design [CAD]/computer-aided manufacturing [CAM] especially) have significantly improved, these still result in larger internal gaps than cast crowns, possibly resulting in thicker cement layers\(^4\) and poorer frictional retention to the abutments. These would be critical challenges for zinc phosphate cement because of its solubility and lack of adhesiveness. Although zinc–phosphate has been indicated for some all-ceramic systems (ca In-Ceram [VITA Zahnfabrik H. Rauter GmbH & Co KG, Bad Säckingen, Germany], Procera [Nobel Biocare, Switzerland], Cercon [DeguDent, Hanau, Germany], Lava [3M ESPE, St Paul, MN, USA]), long-term clinical data are yet to be published.

Glass ionomer cements are also of great interest for clinicians. These cements exhibit several clinical advantages,\(^5\) including physicochemical bonding to tooth structures,\(^5,6\) long-term fluoride release, and low coefficients of thermal expansion.\(^5,7\) However, their low mechanical strength compromises their use in high-stress-bearing areas.\(^5,8\) Glass ionomer cements can be used to cement core-reinforced ceramics such as those also allowed to be cemented with zinc phosphate. However, glass ionomer cements would not suit well for ceramics requiring support from the cement. Therefore resin-based cements have become popular, because they have the potential to address the disadvantages of solubility, support, and lack of adhesion described for previous materials.\(^1\)

Restorative dentistry constantly undergoes changes, and no currently available cement is ideal for all situations. The advent of adhesive luting cements has considerably expanded the scope of fixed prosthodontics. This article will focus on resin-based cements as luting agent for all-ceramic systems, due to the important role the cement plays in the final clinical success of such treatment modality.

### RESIN CEMENTS AND ADHESIVE INTERFACES

Resin cements have become popular clinically because of their ability to bond both the tooth structure and restoration. Bonded indirect restorations constitute a substantial part of contemporary dentistry.\(^9\) The successful use of resin cements depends on several aspects related to the bonding mechanisms to both dental tissues and restorations. The scientific knowledge of the materials currently available as well as the acknowledgment of their limitations and indications are key factors for durable restorations. Several new luting cements and ceramic systems have been introduced in the last few years, and their chemistry and structural characteristics are fundamental to produce an optimal and reliable bonding to both tooth and restoration interfaces.

**Resin Cements: Chemistry and Properties**

Table 1 summarizes various resin-based cements with their respective characteristics and chemical compositions.

Resin-based luting cements were primarily based on acrylic resin chemistry. Their subsequent development, however, has been based on the chemistry of resin composites and adhesives.\(^10\) Currently, several new resin cements are available in the market. These are offered in a wide variety of bonding mechanisms, curing modes, indications, and features (see Table 1). The choice of a particular resin cement requires understanding of the material’s characteristics as well as how it performs individually and integrated in the restorative system. There are two main categories of resin luting cements: the conventional resin luting cements, which have no inherent adhesion to tooth structure and require a bonding agent, and the self-adhesive resin cements, which do not require a separate bonding treatment to the dental substrate.
Conventional resin luting cements

Since the 1970s, resin cements have been formulated based on dimethacrylate resin chemistry as two-paste systems, which are easy to mix and cure at room temperature. Their bonding to tooth structure relies on the use of etch-and-rinse or self-etch adhesives. Composition is usually a mixture of dimethacrylate monomers, inorganic fillers (60% to 70% by weight), and initiator. Silica or high molecular weight oligomers may also be added to modify the rheological properties and achieve optimum handling characteristics. Examples of their clinical applications include metal-based crowns and bridges, zirconia and alumina framed crowns, fiber posts, and cast metal post and core. Because of the importance of light- and dual-curing systems, a separate topic was created to address their clinical application and polymerization mechanisms.

Curing protocols and its clinical relevance

Light-cured Conventional resin cements can be exclusively light-cured. When comparing cements, light-cure products offer the clinical advantages of extended working time, setting on demand, and improved color stability. However, the use of light-cure only cements is limited to situations such as cementing veneers or shallow inlays, where the thickness and color of the restoration do not affect the ability of the curing light to polymerize the cement.11,12

Dual-cured Dual-cured resin cements are often provided in two-paste systems (see Table 1). Dual-cure resin cements are indicated when delivering restorations where material characteristics may inhibit sufficient light energy from being transmitted to the cement.13 In these situations, light intensity reaching the cement may be sufficient to trigger the light-activated polymerization process, but a self-polymerized catalyst is needed to ensure maximal cure. The delivery method usually involves mixing of paste to paste (see Table 1). One of the pastes contains a reducing amine and a photo initiator. The other paste contains peroxide, usually benzoyl peroxide. In an interesting variation of the initiator system, the anaerobic cements begin polymerization only when the ambient oxygen supply is cut off after placement of the prosthetic device. This feature provides extended working and setting times and offers easy removal of excess materials.14,15 Although the dual-curing concept seems to be attractive, several issues have been brought up in the dental literature regarding its performance, and these concerns are going to be addressed throughout the text.

Little has been published on the light-curing potential of dual-cure cements. While earlier research suggests that auto-cure alone is not sufficient to achieve maximum cement hardening,16,17 recent literature indicates that the curing kinetics of dual-cure resin cements is more complex than previously thought.18 Studies indicate that light-activating some dual-cure cements appears to interfere with the self-cure mechanism and restrict the cement from achieving its maximum mechanical properties.19,20 Some dual-cure cements show their self-curing mechanism to be somehow limited when immediately light-activated in the dual-cure mode. This limitation may compromise the final mechanical properties of the resin cements.19 This information is of great importance for the clinical practice, since light activation is always recommended by the manufacturer. It remains to be demonstrated whether the same phenomenon occurs with all resin-based cement systems. While such information is not available, it is advisable to delay the light-curing procedure of dual-cure cements to the maximum time clinically possible.20 In this way, self-curing progress will be further along, to a point when light activation no longer interferes with the self-curing kinetics. The ideal time frame between mixing and the light-activation has not yet been determined, but some studies have shown that light-curing 5 to 10 minutes after mixing
<table>
<thead>
<tr>
<th>Products</th>
<th>Company</th>
<th>Adhesive</th>
<th>Delivery</th>
<th>Curing</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bistite II DC</td>
<td>Tokuyama (Tokyo, Japan)</td>
<td>Primer 1A + 1B/primer 2</td>
<td>Paste/paste</td>
<td>Dual</td>
<td>Silica-zirconia (77% weight) filler, dimethacrylate, MAC-10 (adhesive promoter), initiator</td>
</tr>
<tr>
<td>Calibra</td>
<td>Dentsply/Caulk (Milford, DE, USA)</td>
<td>Prime and bond NT</td>
<td>Paste/paste</td>
<td>Dual</td>
<td>Base: barium boron fluoralumino silicate glass, bis-phenol A diglycidylmethacrylate, polymerizable dimethacrylate resin, hydrophobic amorphous silica, titanium dioxide, di-camphoroquinon Catalyst: barium boron fluoralumino silicate glass, bis-phenol A diglycidylmethacrylate, polymerizable dimethacrylate resin, hydrophobic amorphous silica, titanium dioxide, benzoyl peroxide</td>
</tr>
<tr>
<td>C&amp;B Cement</td>
<td>Bisco (Schaumburg, IL, USA)</td>
<td>All-bond 2 one step</td>
<td>Paste/paste dual syringe</td>
<td>Self</td>
<td>Base: Bis-GMA, ethoxylated bis-gma, triethyleneglycol dimethacrylate, fused silica, glass filler, sodium fluoride Catalyst: Bis-GMA, triethyleneglycol dimethacrylate, fused silica</td>
</tr>
<tr>
<td>Choice 2</td>
<td>Bisco</td>
<td>All-bond one step</td>
<td>Paste</td>
<td>Light</td>
<td>Strontium glass, amorphous silica, Bis-GMA</td>
</tr>
<tr>
<td>Duo-Link</td>
<td>Bisco</td>
<td>All-bond 2 one step/plus</td>
<td>Paste/paste dual syringe; automix</td>
<td>Dual</td>
<td>Base: Bis-GMA, triethyleneglycol dimethacrylate, urethane dimethacrylate, glass filler Catalyst: Bis-GMA, triethyleneglycol dimethacrylate, glass filler</td>
</tr>
<tr>
<td>BisCem</td>
<td>Bisco</td>
<td>Self-adhesive</td>
<td>Paste/paste dual syringe; automix</td>
<td>Dual</td>
<td>Bis (hydroxyethyl methacrylate) phosphate (base), tetraethylene glycol dimethacrylate, dental glass</td>
</tr>
<tr>
<td>Product Name</td>
<td>Manufacturer/Location</td>
<td>Type</td>
<td>Dispensing</td>
<td>Components</td>
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<tr>
<td>NX 3 Nexus</td>
<td>Kerr (Washington, DC, USA)</td>
<td>Optibond solo plus optibond all-in-one</td>
<td>Paste/paste dual syringe; automix</td>
<td>Uncured methacrylate ester monomers, nonhazardous inert mineral fillers, nonhazardous activators and stabilizers, and radiopaque agent</td>
<td></td>
</tr>
<tr>
<td>Maxcem</td>
<td>Kerr</td>
<td>Self-adhesive</td>
<td>Paste/paste dual syringe; automix</td>
<td>GPDM (glycerol dimethacrylate dihydrogen phosphate), comonomers (mono-, di-, and tri-functional methacrylate monomers), stabilizer, barium glass fillers, fluoroaluminosilicate glass filler, fumed silica (filler load 67% weight, particle size 3.6 μm)</td>
<td></td>
</tr>
<tr>
<td>Super Bond C&amp;B</td>
<td>Sun Medical (Grand Prairie, TX, USA)</td>
<td>Monomer/catalyst V/polymer powder</td>
<td>4 drops of monomer/1 drop of catalyst s/1 small cup of standard measuring spoon</td>
<td>Self MMA (methyl methacrylate), 4-methacryloxyethyl trimellitate anhydride (4-META), tri-n-butyborane (TBB- catalyst)</td>
<td></td>
</tr>
<tr>
<td>Clearfil Esthetic Cement</td>
<td>Kuraray (Tokyo, Japan)</td>
<td>Self-etch DC bond system</td>
<td>Paste/paste dual syringe; automix</td>
<td>Paste A: bis-phenol A diglycidylmethacrylate, TEGMA, methacrylate monomers, silanated glass filler, colloidal silica Paste B: bis-phenol A diglycidylmethacrylate, TEGMA, methacrylate monomers, silanated glass filler, silanated silica, colloidal silica, benzoyl peroxide, CQ, pigments</td>
<td></td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Products</th>
<th>Company</th>
<th>Adhesive</th>
<th>Delivery</th>
<th>Curing</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Panavia F 2.0</td>
<td>Kuraray</td>
<td>ED primer</td>
<td>Paste/paste</td>
<td>Dual</td>
<td>Paste A: 10-methacryloyloxydecyl, dihydrogen phosphate, hydrophobic aromatic dimethacrylate, hydrophobic aliphatic dimethacrylate, hydrophilic aliphatic dimethacrylate, silanated silica filler, silanated colloidal silica, dl-camphorquinone, catalysts, initiators Paste B: hydrophobic aromatic dimethacrylate, hydrophobic aliphatic, dimethacrylate, hydrophilic aliphatic dimethacrylate, silanated barium glass filler, catalysts, accelerators, pigments</td>
</tr>
<tr>
<td>Breeze</td>
<td>Pentron Clinical Tech (Orange, CA, USA)</td>
<td>Self-adhesive</td>
<td>Paste/paste dual syringe; automix</td>
<td>Dual</td>
<td>Mixture of bis-GMA, UDMA, TEG-DMA, HEMA, and 4-MET resins, silane-treated bariumborosilicate glasses, silica initiators, stabilizers and UV absorber, organic and/or inorganic pigments, opacifiers</td>
</tr>
<tr>
<td>GCem</td>
<td>GC (Tokyo, Japan)</td>
<td>Self-adhesive</td>
<td>Capsules</td>
<td>Dual</td>
<td>Powder: fluoroaminosilicate glass, initiator, pigment Liquid: 4-MET, phosphoric acid ester monomer, water, UDMA, dimethacrylate, silica powder, initiator, stabilizer</td>
</tr>
<tr>
<td>Embrace</td>
<td>Pulpdent (Watertown, MA, USA)</td>
<td>Self-adhesive</td>
<td>Standard syringe or automix</td>
<td>Dual</td>
<td>Uncured acrylate resins, amorphous silica, sodium fluoride</td>
</tr>
<tr>
<td>MonoCem</td>
<td>Shofu Dental (San Marcos, CA, USA)</td>
<td>Self-adhesive</td>
<td>Paste/paste dual syringe; automix</td>
<td>Dual</td>
<td>Not available</td>
</tr>
<tr>
<td>Cements and Adhesives</td>
<td>317</td>
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<tr>
<td><strong>Multilink Sprint</strong></td>
<td>Self-adhesive</td>
<td>Paste/paste dual syringe; automix</td>
<td>Dual</td>
<td>Dimethacrylates and acidic monomers, barium glass, ytterbium trifluoride, silicon dioxide, mean particle size is 5 μm, total volume of inorganic fillers is ~48%</td>
<td></td>
</tr>
<tr>
<td><strong>Multilink</strong></td>
<td>Ivoclar/Vivadent</td>
<td>Primer A + B</td>
<td>Paste/paste dual syringe; automix</td>
<td>Self</td>
<td>Dimethacrylate and HEMA, barium glass filler, silicon dioxide filler, ytterbium trifluoride, catalysts and stabilizers, pigments</td>
</tr>
<tr>
<td><strong>Variolink II</strong></td>
<td>Ivoclar/Vivadent</td>
<td>Excite adhesive</td>
<td>Paste/paste</td>
<td>Dual</td>
<td>Paste of dimethacrylates, inorganic fillers, ytterbiumtrifluoride, initiators, stabilizers and pigments; (Bis-GMA, triethylene glycoldimethacrylate, urethanedimethacrylate, benzoyl peroxide)</td>
</tr>
<tr>
<td><strong>Rely X ARC</strong></td>
<td>3M ESPE (St Paul, MN, USA)</td>
<td>Adper single bond</td>
<td>Paste/paste; clicker</td>
<td>Dual</td>
<td>Bisphenol-A-diglycidylether dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA), polymer, zirconia/silica filler, filler loading approximately 67.5% by weight, particle size for the filler is 1.5μm.</td>
</tr>
<tr>
<td><strong>Rely X Unicem</strong></td>
<td>3M ESPE</td>
<td>Self-adhesive</td>
<td>Capsules (Aplicap: 0.01 mL; Maxicap: 0.36 mL)</td>
<td>Dual</td>
<td>Powder: glass fillers, silica, calcium hydroxide, self-curing initiators, pigments, light-curing initiators (filler load 72% weight, particle size &lt;9.5 μm); Liquid: methacrylated phosphoric esters, dimethacrylates, acetate, stabilizers, self-curing initiators</td>
</tr>
<tr>
<td><strong>Rely X Unicem</strong></td>
<td>3M ESPE</td>
<td>Self-adhesive</td>
<td>Paste/paste; Clicker</td>
<td>Dual</td>
<td>Glass powder, methacrylated phosphoric acid esters, triethylene glycol dimethacrylate (TEG-MA), silane treated silica, sodium persulfate</td>
</tr>
</tbody>
</table>
It is interesting to note that there is no direct correlation between alterations in the degree of conversion (DC) caused by different curing modes and changes in the mechanical properties of the resin cements.\textsuperscript{19} The lack of linear correlation between DC, properties, and density of crosslink in the polymer has also been reported elsewhere.\textsuperscript{21} However, cements that do not cure properly with light activation or have a compromised self-cure reaction may experience adverse chemical reactions and permeability issues when associated with simplified adhesive systems.\textsuperscript{20} This clinically implies that the longer the resin cement takes to set, the greater will be the chance of adverse effects when coupling resin cements to simplified adhesives. To overcome these problems, clinicians have been advised to use three-step etch and rinse or two-step self-etch adhesives.\textsuperscript{20,22-24} When using these systems, adverse chemical reaction and permeability are prevented by the nonacidic and relatively higher hydrophobic characteristics of the bonding resin that comprise the last step of the application of such systems.\textsuperscript{22} Clinical trials are necessary to demonstrate how these issues may affect the long-term performance of different combinations of adhesives and cements.

Concerns on mixing and working time of dual-cure cements Resin-based cements are formulated to provide the handling characteristics required for particular applications. The setting mechanism of dual-cure resin cements is usually based on redox reaction of benzoyl peroxide with aromatic tertiary amines (represented by catalyst and base paste, respectively). At least one paste contains the light-sensitive compound (camphorquinone [CQ]) responsible for initiating the light-cure setting mechanism. After the pastes are mixed together, and until light is provided, the working time is controlled by the ratio between inhibitors of the self-curing reaction and the amount of peroxide and aromatic tertiary amines. Both inhibitors and peroxides are organic chemical compounds susceptible to degradation upon storage. Therefore, dual-cure resin cements have a limited shelf-life and the setting mechanism of those cements may fluctuate during that time, depending on the conditions of storage that might alter the reactive potential of such components. In vitro evidences indicate that both working time (WT) and setting time (ST) may be significantly altered upon storage,\textsuperscript{19} particularly if the storage temperature is far above the recommended (>\textdegree{} 18\textdegree{}–22\textdegree{}C). In one study, some cements presented shortened WT/ST, while others presented extended WT/ST after the kits were purposely aged for 12 weeks at 37\textdegree{}C.\textsuperscript{19} This occurred because of the instability of the components during storage. Degradation of peroxide would extend the WT/ST, and degradation of inhibitors would shorten them. The implications of such changes on the mechanical properties of the resin cements are yet unclear. However, clinicians handling resin cements with shortened WT may experience some clinical difficulties when luting multiple crowns, for example. Conversely, increased adverse chemical reaction and permeability problems may be expected for resin cements with extended WT and ST used in combination with an acidic and permeable simplified adhesive system. This is mostly because the extended ST allows the uncured cement longer time in contact with the acidic adhesive, thus prolonging the adverse reaction.

Bonding mechanisms and incompatibility issues of dual-cure cements Most adhesive systems used with resin-based cements are simplified adhesive systems, because of clinical trends for reduced steps during adhesive procedures. These simplified adhesives are basically of two types: the etch-and-rinse, single-bottle systems and the all-in-one self-etch adhesives. They are both somewhat acidic and hydrophilic in nature.
During cementation, the acidic groups in the uncured layer of simplified adhesive agents (due to presence of oxygen) compete with peroxides for aromatic tertiary amines of the luting agent, resulting in an acid–base reaction between the adhesive and the resin cement. This reaction minimizes proper copolymerization between the two, and the longer the cement takes to cure, the more extent is the compromising effect.25–27 Additionally, the hydrophilic characteristics of such adhesive systems function as permeable membranes. This hydrophilic behavior permits the flux of water through the adhesive after polymerization.28,29 The presence of water at the interface between the adhesive and the cement compromises the total bonded area and proper polymerization of the cement. Water droplets may accumulate at the interface and then function as stress raisers, leading to failure of the adhesive–cement interface (Fig. 1).28 This permeability problem could be partially solved by the application of an intermediate layer of a relatively more hydrophobic, nonacidic low viscosity resin separating the acidic layer of adhesive from the composite resin cement.28,30 The water that accumulates at the interface derives from the hydrated dentin underneath. The negative effect of such water permeation on the bond strength of resin cements to dentin could be confirmed in vitro studies.28,29 Those studies demonstrated improved bond strengths when the teeth were purposely dehydrated in ascending ethanol series before bonded. As such dehydration of dentin is impossible to achieve in daily practice, clinicians are advised to use less permeable adhesive systems such as three-step etch and rinse or two-step self-etch when bonding self- or dual-cured resin cements to dentin.28,30 The major advantage of these systems is that they include a layer of a relatively more hydrophobic and nonacidic resin as the third or second step. This additional layer will not cause adverse reaction with the basic amines of the cement and will reduce the permeability of the adhesive layer.31,32 The incompatibility issue has brought up concerns for several clinical procedures. The worst clinical scenario would occur when luting posts using simplified adhesives associated with dual-cured resin cements (see Fig. 1). Proper bonding to the apical portion might be severely compromised by the adverse interactions between adhesive and luting composite due to a lack of light exposure. Without light activation, dual-cure resin cements will actually function as exclusively self-cure cements. In this mode, the cement will take longer to cure, and this allows more time for the adverse reaction and transudation of water from dentin to occur. A similar situation occurs when the cement takes longer to set because of alterations in the WT/ST caused by inadequate storage conditions, as described previously. Based on those limitations, some studies have suggested the development of a specific bonding system for this purpose.31,32 Recent studies have shown that the push-out resistance of posts luted with resin cements was similar, regardless of the use of adhesive systems to bond to root dentin.31,32 A more predictable, truly adhesive luting procedure can only be achieved when clinicians combine the use of resin cements with three-step etch and rinse or two-step self-etch bonding systems. Self-adhesive resin cements have been strongly recommended to lute posts and crowns as an alternative to conventional luting systems, avoiding incompatibility and permeability issues due to wrong combinations of adhesives and cements.

When cementing inlays, onlays, and crowns, immediate dentin sealing concept33 may be a useful clinical alternative to overcome the incompatibility and permeability issues. Further details on this approach can be found elsewhere.20,34,35

**Self-adhesive resin cements**

The simplification to only one step of resin luting procedures was achieved with the self-adhesive resin cements.36 This system uses a dual-cure concept for polymerization, and no pretreatments using bonding agents on the tooth surface is required,
making its application clinically attractive. Self-adhesive resin cements are claimed to be moisture-tolerant, to release fluoride, and to present no postoperative sensitivity. Thus, all these factors combined fit to the clinical demand for simplification and less technique sensitiveness.

Fig. 1. This sequence of micrographs shows the in vivo morphologic characteristics of root dentin during postcementation procedures using an etch-and-rinse two-step adhesive system. Observations were made in (A) cervical, middle, and apical thirds (dotted circles) of the root canal by means of an impression with a polyvinyl siloxane material taken immediately after (B) postspace preparation, (C) etching with phosphoric acid, and (D) application of the adhesive system. The impression of the root canal was then positioned in a container allowing an epoxy resin to be poured covering up to half of the impression. After gold sputtering, the samples were taken to a scanning electron microscope at 1000 × magnification for evaluation. After postspace preparation, the anticipated presence of a smear layer (arrows) was observed in the (Bc) cervical and (Bm) middle thirds, but noticeably higher amounts were detected at the apical section (Ba). Remarkably, etching with phosphoric acid did not effectively remove the smear layer at either cervical, middle, or apical thirds (Cc, Cm, Ca, respectively), and dentinal tubules do not seem to be available for hybridization. Micrographs taken after subsequent layering of an adhesive system with a microbrush revealed evidence of water permeation and blistering (pointers) protruding from the dentin surface, and they were more frequently observed in (Dc) cervical and (Dm) middle thirds relative to the (Da) apical third. One possible reason may be the progressively lower number and diameter of dentinal tubules toward the apical area and the reduced permeability in this area.

making its application clinically attractive. Self-adhesive resin cements are claimed to be moisture-tolerant, to release fluoride, and to present no postoperative sensitivity. Thus, all these factors combined fit to the clinical demand for simplification and less technique sensitiveness.
The first of this class of materials was introduced as a powder–liquid material provided in unit–dose capsule that had to be triturated (RelyX Unicem [3M ESPE, St Paul, MN, USA]), and newer paste-paste versions have been commercialized (see Table 1). The setting reaction is initiated by light exposure and by the self-curing mechanism. In general, the initial low pH is neutralized through reactions between acid groups and alkaline filler and tooth apatite. Lower bond strengths to enamel compared with dentin have been reported, and this fact may limit the use of self-adhesive resin cements for bonding veneers.\textsuperscript{15,38} Moreover, esthetic veneers and minimally invasive restorations require longer working time for positioning and demand more esthetic and shade availability than the ones that have been provided for self-adhesive kits.

**Bonding mechanism of self-adhesive cements** Conventional resin cements require an adhesive agent to mediate bonding to tooth structure, which can be either etch-and-rinse (three- or two-step) or self-etch adhesive system (two- or one-step). It seems that the more steps involved in the bonding procedure for both bonding approaches, the more stable is the bonded interface produced.\textsuperscript{39} Conversely, when more clinical steps are required, it is also more critical to keep the bonding substrates properly isolated; additionally the chances are higher for technique sensitivity.

Self-adhesive resin cements do not require the bonding step. The acidity of the cement is strong enough to promote hybridization with the tooth structure. While still fluid, the acidic groups of the monomer dissolve the smear layer, which allows penetration of the cement into the dentinal tubules, thus providing a good hybrid layer and good adhesion. Micromechanical retention and chemical interaction between acidic groups and hydroxy-apatite are expected. It has been reported that self-adhesive cement showed chemical interaction with Ca ions derived from hydroxy-apatite.\textsuperscript{40} Enamel bonding with a self-adhesive cement produced lower bond strengths than conventional resin cements but higher than glass–ionomer. It may be considered as an alternative to glass–ionomer luting cement for cementation of high-strength ceramic or metal-based restorations, but it might not be ideal for luting restorations such as veneers, inlays, and partial crowns if a considerable enamel surface area is present.\textsuperscript{41} The use of phosphoric acid for etching enamel before the application of self-adhesive resin cement can result in bond strengths comparable to conventional resin cements.\textsuperscript{42} However, previous etching can be detrimental for bond strengths to dentin.\textsuperscript{43} Although self-adhesive and conventional resin cement–dentin interfaces are morphologically different,\textsuperscript{43,44} self-adhesive cements have been reported to perform equally effective when compared with most conventional resin cements.\textsuperscript{38,45,46} There is still a need for a more long-term clinical evaluation of self-adhesive cements.

**Resin Cement and Water Sorption Phenomenon**

When an all-ceramic crown is cemented, the assembly ceramic/cement/adhesive/tooth will be subjected to a watery environment. Resin cements should not only have low solubility, but also low water sorption because of esthetic and functional reasons.\textsuperscript{47} The water sorption phenomenon has been demonstrated to have an important effect on the properties of resin cements after long periods of time.\textsuperscript{48,49} Water sorption diminishes significantly the flexural strength of resin composites. The reduction of flexural strength as well as modulus of elasticity\textsuperscript{50} may be critical for thick areas of resin cement. Scientific evidences show that absorbed water works as a plasticizer for the cements and, therefore, may create unsupported areas underneath restoration and consequently increase the chance of fracture of the restoration under mastication
forces. Clinicians should keep as thin as possible the cement film to minimize the consequences of the plasticizing phenomenon for resin cements. The water sorption may also result in hygroscopic expansion of the cement, but the consequences of hygroscopic expansion on the long-term durability of dental cements, and consequently all-ceramic restoration, remain unknown.

Clinicians should be aware that cements that present extended working time or setting time, do not cure properly with light activation, or have a compromised self-cure mechanism will more severely suffer with hygroscopic expansion issues. Incomplete polymerization and nonconversion of monomer may result in loss of resin, and this may affect the biologic compatibility of the resin material. Scientific evidence has demonstrated that reducing the exposure time for polymerization of light-cure cements to 75% of that recommend by the manufacturer may facilitate fluid uptake and dissolution of the resin. Therefore, all measures should be taken to permit maximum polymerization of resin cements to minimize the water sorption phenomenon and its consequences.

Vrochari and collaborators have recently evaluated water sorption and solubility of several cements. The authors observed that materials with similar polymerization mechanisms may perform differently during their interaction with water. Thus, clinicians are advised to be aware whether the resin-based cements to be chosen follow the International Organization for Standardization (ISO) standards regarding water sorption performance. Ideally, resin cements should present the lowest water sorption and solubility values possible.

**Film Thickness of Resin-Based Cements**

The importance of resin cement film thickness currently relies on the fact that most of the ceramic materials have considerable internal space. The effect of resin cement thickness on the fracture resistance of all-ceramic restorations is not completely established yet, but some studies have found some correlation between these factors. In 1994, Scherrer and colleagues reported that when resin cement thickness of 300 μm or more was present, a gradual decrease of the fracture strength was observed demonstrating that thick ceramic combined with minimal thickness of luting composite provided restorations with a favorable configuration with regard to prevent cracking. It was also demonstrated that glass–ceramics with thick cement layers exhibit significantly lower reliability after water aging. It seems that a thin cement thickness and proper bond to the ceramic structure is necessary for improved support and increased fracture resistance of all-ceramic crowns. Thicker cement layers have also been related to decreased bond strength of ceramic systems. Thus, clinicians are strongly advised to maintain a minimal film thickness (approximately 50 μm) to minimize the effects of water sorption and its consequences to the properties of the cement and respective support for the ceramic restoration.

**BONDING INTERFACE OF ALL-CERAMIC MATERIALS**

The development of new cement and adhesive techniques expanded the use of ceramics and indirect resin composites in dentistry. Bonding ceramic materials to enamel and dentin combined with the improved strength of these indirect restorative materials has produced restorations with improved mechanical integrity and reduced risk for fracture. Although a separate article of all-ceramic systems is included in this special issue for Dental Clinics of North America, a brief description of the ceramic materials characteristics will be presented to favor the understanding of their bonding strategies and mechanisms at the resin–cement/restorative material interface.
Glass Ceramics

Feldspathic glasses and Leucite-containing feldspathic glasses are still extensively used in veneers, inlays, and single anterior crowns. They offer excellent esthetic outcomes derived from their high translucency, fluorescence, and opalescence. However, these ceramics have drawbacks such as reduced strength and toughness. The glass–ceramic systems currently available are:

- Leucite-reinforced glass-ceramics (sintered, hot-pressed or CAD-CAM) with flexural strengths of up to 120 MPa, which is considered to be sufficient for veneers, anterior crowns and posterior inlays
- Fluornica glass-ceramics (CAD-CAM) with flexural strength of 120 to 150 MPa, which, combined with the adhesion to tooth tissues, may be adequate for selected posterior crowns.

A significant improvement of the mechanical properties (flexural strength around 350–450 MPa) of glass–ceramic systems was achieved with the development of lithium disilicate glass–ceramics (hot-pressed or CAD-CAM). Since the introduction of lithium disilicate ceramic to the market, the use of Leucite-reinforced glass–ceramics has declined. Moreover, besides the better mechanical properties and improved esthetic outcomes, high bond strength can be achieved when bonded to the tooth structure.60

High-Strength Polycrystalline Ceramics

Although high-strength polycrystalline ceramics (alumina and zirconia) broaden the applications of all-ceramic systems to posterior crowns and bridges, randomized clinical trials and clinical experience have been controversial regarding long-term survival.61–67 As a result of its superior mechanical properties compared with alumina, zirconium became the first choice as a core or framework for all-ceramic restorations. However, it is imperative to mention that the bonding mechanisms to high-strength ceramics have been problematic as a result of lack of glass particles in its composition. This issue and possible adhesion options to high-strength ceramics are discussed in detail throughout the following section.

Bonding strategies for all-ceramic systems

The ability of a combination of resin cement/adhesive system to adhere to dental ceramics depends on the microstructure of the esthetic restoration and the surface treatment applied.68 While roughening the surface by grinding or airborne particle abrasion is considered a way for improved adhesion for most of the esthetic materials, silanation appears to be only effective for silica-based ceramics.69 A durable and reliable bond for dental resin-bonded ceramics is usually attempted via two principal mechanisms: (1) micromechanical attachment to porosities originated from hydrofluoric acid (HF) etching or (2) grit blasting, associated with a silane-coupling agent. Evaluations of bond strength between ceramic and resin composite have derived different conclusions about the effect of surface treatments. Controversy in the literature70,71 relies on possible inefficacy or inactivity of the silane-coupling agent applied and operator’s handling of the procedure. Meng and colleagues72 recently demonstrated that hydrofluoric acid treatment could enhance the bond durability of resin/silanated glass ceramics, which might result from the increase of the chemical adhesion area on the ceramic rough surface and subsequently reduced degradation speed of the silane coupler, rather than the mechanical retention of the ceramic rough surface.72
Silane coupling

Silane-coupling agents are bi-functional molecules capable of bonding to the hydroxyl groups on ceramic surfaces and copolymerizing with the organic portion of the resin cement or adhesive. Silane primers contain a silane agent (usually γ-methacryloxypropyl-trimethoxy silane), a weak acid, and high amounts of solvents. To be effective, the silane agent must be hydrolyzed by the weak acid. Once hydrolyzed, silane primers have a limited shelf-life, and effectiveness progressively decays over time. The effectiveness of prehydrolyzed, single-bottle silane primers is, therefore, unpredictable if the user is not aware of when the solution was activated. Clinically, the only indicator seems to be the appearance of the liquid (i.e., a clear solution is useful, while a milky-like solution should be discarded). However, alcoholic solution (one-bottle systems) stays transparent, and the signs of alterations cannot be identified. Therefore, two-bottle solutions are preferred. Practitioners should strictly respect expiration date and follow the manufacturers’ recommendations of silane systems.

The understanding of how the silanation process occurs on ceramic surfaces is of great importance to improve effectiveness of silanes. When a silane is applied to a ceramic surface and dried, three different structures are formed at what is called interphase layer. The outermost layer consists of small oligomers that can be washed away by organic solvents or water at room temperature. Closer to the glass surface, there is another layer of oligomers that is hydrolysable. To avoid hydrolysis of this layer after cementation, which could compromise the coupling of the cement with the ceramic, some authors recommend it be removed with hot water before bonding to silanated ceramic. Attached to the glass there is a third layer, which is a monolayer that is covalently bonded to the silica phase of the ceramic and is hydrolytically stable. This remaining monolayer of silane is not removed by these procedures, and it is responsible for the actual bond between the ceramic and the adhesive/cement system.

Since it is not possible to clinically control the application of a monolayer of silane, undesirable excess must be removed before bonding. This can be achieved by several methods. One way is to apply the silane followed by hot air drying (50°C ± 5°C) for 15 seconds for proper solvent evaporation. Then, rinse with hot water (80°C) for 15 seconds followed by another hot air drying for 15 seconds. This procedure would eliminate water and solvent and wash away any unreacted silane (excess) primer components. Alternatively, excess silane can be removed during the try-in step. The try-in procedure is known to be a contaminant step. Therefore, it has been recommended to be done before silanation. Clinicians generally use the try-in step after receiving the surface-etched (hydrofluoric acid, HF) ceramic restoration from dental laboratories. However, the HF-treated ceramic surface is hydrophilic and more prone to be contaminated if the hydrophilic try-in paste is applied before the silanation step. Therefore, ceramic surfaces should be silanated before the try-in procedure. Once properly silanated, the ceramic surface becomes hydrophobic, and the try-in paste can be easily removed by ultrasonic cleansing. Current scientific evidences show that if the try-in step is done after silanation, bond strengths will increase significantly. This can be explained by the fact that the try-in procedure removes the excessive layers of silane from ceramic surface. The removal of excess permits proper coupling of the resin cement with the monolayer-silanated ceramic surface, thus improving the bond strength. Moreover, silane treatment alone seems to be very effective to improve bond strengths to ceramic. Thus, when the try-in step is involved, it should rather be done after silanation, followed by ultrasonic cleanse for better bond strength.

A durable bond with high-strength polycrystalline ceramic systems has been proved to be a difficult task. The use of a silane-coupling agent after airborne particle abrasion
(APA) did not result in a durable resin bond to zirconium. As an alternative, silicoating has been proposed to create an additional silica layer over the reinforced ceramic cores to allow for bonding procedures. However, some reports demonstrated a significant reduction in the bond strength after simulated artificial aging in zirconium-based ceramics treated with silicoating followed by silanization. Reinforced ceramic core systems are not as dependent on bonding as the fragile feldspathic ceramics. Manufacturers’ recommendations for luting reinforced ceramic cores suggest the use of conventional cements such as zinc phosphate or resin-modified glass ionomer. However, adhesive cementation has been shown to increase its fracture resistance and longevity; sealing of internal surface flaws created by airborne particle abrasion (APA); and working as auxiliary retention to its inherent loose fit.

Many different chemo-mechanical surface treatments have demonstrated effectiveness in optimizing the cement/reinforced ceramic bonding interface. Slight differences in the sintering temperature may influence the final poly-crystal structure, grain sizes, and mechanical properties. Thus, different ceramics reactions to specific surface treatments may be expected. Several studies have investigated if these treatments, combined or not, can promote more durable bonds to reinforced ceramic cores. Among them, there is airborne particle abrasion (APA) or wet hand grinding, use of phosphate ester and phosphoric acid monomers present either in resin luting cements or some primers; tribochemical silicoating, laser irradiation, selective infiltration–etching (SIE) technique by heat treatment, and others. To date, however, there is no clinical consensus regarding the best surface conditioning method for achieving optimum bond strength to reinforced ceramics. Despite these invaluable efforts, the clinical significance of bonding to high-strength ceramics and its influence on the long-term survival warrants future investigation.

APA APA or wet hand grinding is an alternative widely investigated for improved resin bonding to reinforced ceramics. Some research groups have demonstrated that these mechanical surface modifications significantly increased the flexural strength of Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) by inducing a tetragonal to monolithic phase transformation that could inhibit microcrack extension, thus increasing the strength of zirconium. Conversely, other scientific evidences are showing that surface treatments such as grinding or sandblasting Y-TZP ceramics before cementation may create surface defects and sharp cracks that can be stress concentration sources that render the zirconium framework susceptible to radial cracking during function. Significantly lower reliability for zirconium core ceramics was demonstrated for two postsintered cementation surface modification techniques, grinding and alumina abrasion, when compared with the as-received zirconium cores. In 2005, Guazzato and colleagues detected a significant amount of monoclinic phase (9.5%) after sandblasting but no monoclinic phase detection after heat treatment. Authors assumed that the compressive stresses created were released, and the mean flexural strength obtained was related to the defects induced by sandblasting without the benefits of the transformed region. Thus, they assumed that any temporary beneficial effect induced by different surface treatment methods could be counteracted by fatigue-related crack growth phenomena.

Low-pressure air abrasion (0.05 MPa) was proposed as an alternative to improve bond strength without compromising the ceramic structure. The authors of both studies stated that although the surface roughness was reduced, it did not affect the long-term bond strength. However, omitting air abrasion resulted in debonding during artificial aging, independent of using primers. In 2010, Aboushelib and colleagues demonstrated that APA specimens may have their flexural strength...
recovered by the application of the bonding agent. Standard error of the mean analysis of the fractured surfaces indicated that application of the bonding agent resulted in sealing of the surface damage produced by APA. Additionally, Casucci and colleagues\(^82\) (2010) evaluated the surface roughness for three different ceramics and a significant increase in the average surface roughness of Cercon (DETREY DENTSPLY) (DeguDent, Hanau, Germany) and Aadva (GC Corporation, Tokyo, Japan) Zr ceramics were found, while no differences were produced on Lava (3M ESPE, St Paul, MN, USA). Thus, manufacturers’ recommendations must be taken under consideration regarding APA and wet grinding mechanical surface modification, because ceramics perform differently in response to the same APA approach.

Resin cements and primers containing 10-MDP monomer (10-methacryloyloxydecyl dihydrogenphosphate) have been considered the materials of choice because of the chemical interaction established between the hydroxyl groups of the zirconia ceramic and the phosphate ester monomer of the MDP-containing material.\(^94,95\) Resin luting cements as Panavia,\(^96\) and some primers as Alloy Primer, Clearfil Ceramic Primer (Kuraray, Osaka, Japan) are representatives of this type of material. The use of zirconia 10-MDP-based primers in combination with APA improved resin bond strength, immediately and in long-term evaluations.\(^78,83,91,97,98\) However, more recently, Aboushelib and colleagues\(^93\) observed bond strength reduction after artificial aging for the APA group in combination with application of MDP monomer. Authors\(^93\) related the contradiction to the fact that their study used microbars instead of discs, which expose more surface area of the bonded interface to the influence of water. Primers containing phosphoric acid monomer as Metal/Zirconia Primer (Ivoclar-Vivadent) and AZ Primer (Shofu) are also considered alternative to promote the adhesion to oxide ceramics such as zirconia and alumina, because they are claimed to achieve chemical bond to the oxidic ceramic surface.\(^91,97\) Differences in chemical composition of the primers and their bonding mechanisms require adequate combination of surface treatments and the proper selection of primer according to each commercial resin cement system.\(^98\) In general, primers containing a phosphonic acid monomer or phosphate ester monomer improve resin bonding to zirconia ceramics, while primers containing a silane-coupling agent improve resin bonding to silica–base ceramics.\(^97\) A new zirconia experimental primer, based on a mixture of organophosphoric and carboxylic acid monomers, has been recently investigated as another alternative to increase bond strength of different resin-based luting agents.\(^99\)

**Tribochemical silicoating** Tribochemical silicoating has been claimed as an alternative to APA, in an attempt to improve the bond between alumina/zirconia ceramics and resin cements.\(^100\) In this technique, the surfaces are airborne-particle abraded with aluminum trioxide particles modified with silica. The blasting pressure results in the embedding of the silica-coated alumina particles on the ceramic surface, rendering the silica-modified surface chemically reactive to the resin through silane-coupling agents. Some studies have demonstrated high bond strength values of resin to zirconia after silicoating and silanation.\(^83,101\) However, when artificial aging was proposed, it resulted in significant decrease in bond strengths of resin to silicoated zirconia.\(^76–78\) The authors further indicated that thermal cycling had a greater impact on the durability of the resin bond to zirconia ceramic than water storage at constant temperature.\(^76–78\)

**New approaches to enhance bonds to high-strength polycrystalline ceramics** A newly developed surface treatment has been proposed to improve zirconia bonding, the selective infiltration etching (SIE) technique by heat treatment.\(^93\) It transforms the zirconia from a dense, nonretentive, and low-energy surface to a highly active and retentive surface. In this procedure, the surface is coated with a glass-containing
conditioning agent (composed of silica, alumina, sodium oxide potassium oxide, and titanium oxide) and heated above its glass transition temperature. After cooling, the glass is dissolved in an acidic bath, creating a porous surface and achieving promising results in terms of bond strength to resin cements. In 2010, Aboushelib and colleagues\textsuperscript{93} demonstrated that SIE established a strong, stable, and durable bond to zirconia substrates as well. Stanard error of the mean analysis demonstrated that the surface topography created a highly retentive surface where the adhesive resin penetrated and interlocked. Even though the depth of resin tags was limited to $0.3\,\mu m$ to $0.7\,\mu m$, the porosities allowed for the establishment of a strong nanomechanical bond with the adhesive resin used, which resisted nanoleakage during artificial aging.\textsuperscript{93}

Alternatively, laser irradiation has been introduced as another treatment option for zirconia and alumina surfaces. Er,Cr:YSGG laser should be considered an innovative alternative for promoting adhesion of ceramics (glass-infiltrated alumina) to resin cement, since it resulted in similar bond strength values compared with the tribochemical treatment.\textsuperscript{102} Also, CO\textsubscript{2} laser etching may represent an effective method for conditioning zirconia surfaces, enhancing micromechanical retention, and improving the bond strength of resin cement on zirconia ceramic.\textsuperscript{84}

**SUMMARY**

Clinical trials are required to understand what the real performance of new ceramics in the oral environment may be and what the role of luting agents and surface treatments on their performance may be. In addition, many other individual factors are involved in a clinical failure, such as core design and thickness and damage by processing and handling, added to the occlusal function. The high number of clinical complications with all-ceramic fixed dental prostheses, even with increased connector size,\textsuperscript{103} requires clinical attention in the material selection, and an important improvement of the veneering system is still required.\textsuperscript{104} Up to date, there are a limited number of published clinical trials on Y-TZP and other reinforced core ceramics, but it has the potential for being accepted as a suitable material for fixed prosthodontics.\textsuperscript{105}

In addition, it is important to evaluate the long-term performance of different surface treatments. Other approaches are expected to be developed to improve/stabilize the bonding mechanisms to teeth and all-ceramic systems involving, for instance, chemical function of the tooth and ceramic substrates via increase of the amount of $-OH$ groups and consequently the wet ability response on the surfaces prior bonding, potentially enhancing the long-term expectation of ceramic/cement/substrate interface.

**ACKNOWLEDGMENTS**

The authors thank Dr Van Thompson, chair of the department of Biomaterials and Biomimetics at New York University College of Dentistry for his guidance and editorial support.

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