ADHESIVES AND HYBRIDS

Adhesive Bonding to Hybrid Materials: An Overview of Materials and Recommendations

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Abstract: Recently, hybrid materials have been introduced to the dental market. Together with computer-assisted design/computer-assisted manufacturing (CAD/CAM) composite resins, they form a new class of dental CAD/CAM materials that combine the positive effects of ceramics and composites. As bonding is essential for their clinical longevity, it is crucial to have a good understanding of their material properties and cementation protocols. This review offers clinicians an overview of available hybrid materials and recommendations for their respective adhesive placements.

In the last decade, computer-assisted design/computer-assisted manufacturing (CAD/CAM) technology has become increasingly popular and fulfills higher patient expectations with regard to more natural and esthetic tooth-colored indirect restorations. In addition to the time-efficient working process, reduced laboratory time, and economic benefits for both patient and clinician, the use of CAD/CAM technology facilitates quality control and the utilization of new materials.[1] Today, a large variety of CAD/CAM materials is available, from resin composite and silica-based ceramics to high-strength ceramics.

Hybrid materials have recently been introduced to the dental market and form a new class of CAD/CAM materials. These new ceramic/polymer materials, or polymer-infiltrated ceramic-network materials, combine the positive aspects of both ceramics and composites with their respective beneficial mechanical properties.[2]

Adhesive bonding is essential for ceramic restorations and can enhance their clinical long-term success.[2] Furthermore, it can minimize microleakage, ensure marginal adaptation, and improve fracture strength of both the tooth and indirect restorations.[3,4] However, adhesive cementation is a double-sided process. The pretreatment steps of dental hard tissues and the individual surface-treatment methods for each ceramic material must be considered.

Bonding inorganic restorations to organic and vital tooth tissues remains challenging. To cope with this, much ingenuity has been necessary. In the mid 1950s, Buonocore[5] was the first to make adhesive dentistry possible with the introduction of acid etching on enamel. Until then, sound tooth structures needed to be removed to enhance the retention and stabilization of dental restorations. Little progress was made in later years. In contrast to enamel bonding, dentin bonding was still unsatisfactory. In the late 1970s, Fusayama[6] implemented the total-etch technique, and in 1982, Nakabayashi and colleagues[7] first described the formation of the hybrid layer in dentin, which is essential for proper adhesive bonding. The goal of succeeding researchers was to simplify the time-consuming multistep bonding procedures to the recent one-step adhesives.

Today's adhesive systems can be classified according to the number and combination of pretreatment steps needed to etch and rinse (total-etch) adhesives, with multiple pretreatment steps (three-step and two-step systems) of enamel/dentin and self-etch materials (two-step and one-step adhesive systems).[8]

The so-called "universal," "multipurpose," or "all-in-one" adhesives are said to be the ultimate bonding materials in terms of ease of application and time needed. However, some consider the etch-and-rinse technique with multiple bottles as the gold standard in enamel pretreatment and some authors recommend it for indirect restorations.[8] For dentin, the use of self-etch adhesives is a well-accepted method[8,9] and considered by some to be the first choice for direct composite treatments.[10] Both processes are indicated for different clinical situations, balancing their pros and cons in each case.[11]

Adhesive Cementation

Resin Cements for Indirect Restorations

Over time, resin cements have proven to be successful and have become widely popular due to their abilities to bond to both dental hard tissues and indirect restorations.[12] Furthermore, adhesive cements are characterized by good mechanical retention and superior esthetics.[13] Contemporary resin luting agents can be divided according to their polymerization reactions into light-curing, chemical-curing, and dual-activated[4] cements, or by how their adhesive systems operates—total-etch, self-etch, and self-adhesive.[14]

Light-curing resin cements demand a beam of light to initiate their chemical-curing reactions. These cements are predominantly used for restorations in the esthetic zone. Every part of the cement line must undergo adequate light curing. Both ceramic thickness and opacity of the restoration can influence the polymerization: a maximum occlusal thickness of 3 mm and a maximum approximal thickness of 6 mm is recommended when only light-curing systems are used.[15] Otherwise, failure due to insufficient curing will likely occur.[14] Dual-curing systems, however, can cure with or without the activation of light, as they contain chemical self-cure initiators to start polymerization. Nevertheless, a stronger bond can be achieved with additional light curing, resulting in better marginal adaption.[16] In areas in which not enough light transmission can be achieved, the use of chemically activated resin cements is advisable, as the curing reaction starts immediately and independently after application. This class of cements is especially indicated in posterior regions, for opaque restorative materials, and for posts.[14]

Every system has its respective advantages and disadvantages. In general, the use of resin luting agents offers significant advantages, such as providing predictably high durable bond strength values and a wide spectrum of indications. In addition, adhesive luting is strongly recommended for minimally invasive ceramic restorations, such as veneers, inlays, and partial crowns.[4,17] However, adhesive cementation can be technique sensitive, and marginal discoloration of the cementation joint can occur with time, which can be a major factor in esthetic cases. Moreover, their flowable consistencies can make removal of excess cement difficult.

Self-adhesive cements were developed to simplify the bonding process. These cements can be used in a single step, without prior pretreatment of dental hard tissues.[12,14] Nevertheless, in vitro studies[10,13,18,19] have shown that using complex multi-bottle systems for total-etch and self-etch applications is still superior to employing simple self-adhesives.


Fig 1.

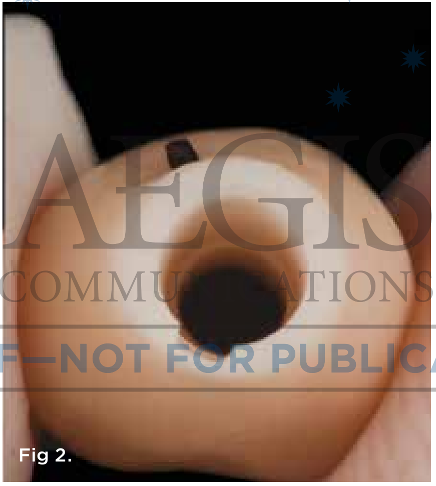
Fig 2.


Fig 3.


Fig 4.


Fig 5.


Fig 6.

Fig 1 to Fig 3. Pretreatment steps of a hybrid ceramic implant crown: (A) etching, (B) visible etching pattern, and (C) silanization. **Fig 4 to Fig 6.** Cementation process (A to C) of a hybrid ceramic implant crown on a titanium abutment.

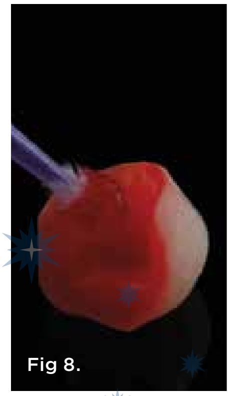

Fig 7. Final restorations. **Fig 8 to Fig 10.** Pretreatment steps of hybrid ceramic: (A) hydrofluoric etching, (B) visible etching pattern, and (C) application of silane. **Fig 11.** Etching pattern of hybrid ceramic under scanning electron microscope after etching with hydrofluoric acid for 60 seconds.

Surface Treatment of Indirect Restorations

Independent of the type of resin cement used, numerous studies have revealed that the surface treatment of ceramics prior to bonding has a strong impact on their bonding behaviors.[4,20-22] An increase of the surface roughness and proper surface activation of indirect restorations through various surface treatments provides better mechanical interlocking and a stronger bond to the cement.[4] Different surface-treatment methods have been tested in many in vitro studies.[23-25]

The optimal surface-conditioning protocol described for silica-based ceramics is hydrofluoric (HF) acid etching, followed by an application of a silane.[4,26] Hydrofluoric acid selectively dissolves the glass components, thus resulting in an enlarged surface texture with microporosities for mechanical retention.[11] Silane, moreover, enhances the wettability and builds strong chemical siloxane bonds to the etched porcelain surface.[11] A recently published review by Kern[27] summarized and compared the current clinical and laboratory scientific evidence on the proper bonding behavior of high-strength oxide ceramics. He stated that, for both glass-infiltrated alumina and zirconia, air-particle abrasion at a moderate pressure and application of a 10-methacryloyloxydecyl dihydrogen phosphate (MDP)-containing resin luting agent can be recommended for clinical long-lasting success. The MDP monomer is essential, as it provides a durable chemical bond to oxide ceramics.[27] Furthermore, the concern regarding weakening oxide ceramics with the application of air-particle abrasion could be refuted with clinical long-term data. Nonetheless, air-particle abrasion needs to be performed at a moderate pressure rate. In contrast to zirconia, silica-based ceramics and lithium disilicate should not be air abraded, as this process can induce crack formation and bulk failure.[4]

Air-particle abrasion, along with additional silane application, also showed higher bond strength values to laboratory-fabricated composites.[2] The created irregularities lead to a higher surface roughness and surface energy,[2] and to better mechanical interlocking to the composite.[28]

Hybrid Materials

These new types of materials may be mainly divided into two subgroups according to their chemical compositions: those that consist mainly of resin matrix will be referred to as *CAD/CAM composite resins*, and materials that are predominantly based on ceramic will be called *hybrid ceramics*. Another recently published classification distinguishes between ceramics and ceramic-like materials, placing them in three groups: glass-matrix ceramics, polycrystalline ceramics, and resin-matrix ceramics.[29]

The only available CAD/CAM hybrid ceramic,[2,30] VITA ENAMIC® (VITA Zahnfabrik, vita-zahnfabrik.com) is comprised of two double interpenetrating parts: a ceramic, which is comprised of an aluminum oxide–enriched, fine-structure feldspar matrix (86 wt%) and a polymer (14 wt%), which contains urethane dimethacrylate and triethyleneglycol dimethacrylate.[30]

Due to the synergy of the ceramic and polymer components, the material shows good edge stability (in the sense of good machinability with thin edges) for minimal layer thickness, economical machinability, and less brittleness when compared with conventional ceramic materials.[30,32,33] The material covers all indications for minimally invasive dentistry and is approved for use in inlays, onlays, full crowns, and screw-retained implant crowns.[34] Furthermore, hybrid materials have been recommended for vertical dimension changes in the occlusion.[30,33]

Yet, no controlled clinical studies have been published. To date, only an abstract of a scientific poster of a clinical prospective 5-year study of minimally invasive hybrid ceramic CAD/CAM restorations is available. The authors reported a promising survival rate of 100% after an observation time of 1 year.[34] However, further clinical long-term data are needed to confirm these preliminary results.

Other innovative new CAD/CAM resin composites are Lava™ Ultimate (3M ESPE, 3mespe.com) (a resin-based block nanocomposite),[35] CERASMART™ (GC America, gcamerica.com), and SHOFU Block HC (SHOFU Dental, shofu.com). Lava Ultimate consists of nanoceramic particles embedded in a highly cured resin matrix.[36] It is defined as a mixture of both composite and ceramic[37] and labeled by the manufacturer as a resin nanoceramic. CERASMART is a nanoparticle-filled high-density composite resin, which contains 71% of filler particles by weight.[38] SHOFU HC is available both as a block and a disk for industrial-scale milling machines and consists of silica powder and zirconium silicate in a resin matrix.[39] The flexural strength of Lava Ultimate and SHOFU HC is 170 MPa to 180 MPa and for CERASMART 220 MPa to 240 MPa,[38,40] which is slightly higher than feldspathic ceramics. All three materials cover nearly the same clinical application spectrum for single restorations and show similar mechanical properties to hybrid ceramics, such as minimum wall thickness and edge

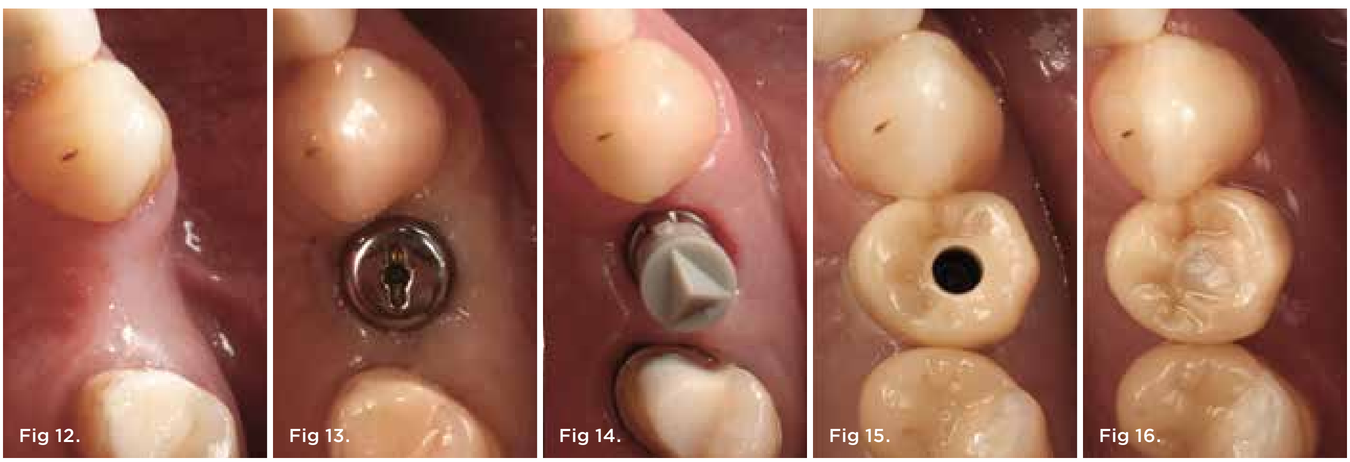

Fig 12 to Fig 16. Clinical case of a minimal invasive CAD/CAM solution with a hybrid ceramic in the posterior region: (A) initial clinical situation, (B) after implant placement, (C) preparation and scan post—ready for an optical impression, (D) cemented restoration and screw-retained implant crown, and (E) treatment result after insertion.

stability.[30] However, 3M ESPE has recently withdrawn the crown indication for Lava Ultimate because of a reportedly high debonding rate.[41,42] This was observed in a clinical study by Schepke et al[43] on cemented implant crowns. A potential explanation may be the low flexural modulus of 12 GPa and a consequent bending of the restoration under load.[43] Furthermore, at launch, surface treatment via air-particle abrasion was not yet recommended.

In a recent study by Awada and Nathanson,[38] it was shown that hybrid materials tended to be less brittle and more flexible compared to conventional ceramics. In addition, more accurate margins could be milled, while fewer flaws and irregularities were observed. It was, therefore, concluded that nonoptimal preparation designs and minimal tooth reduction could be better tolerated.[38]

Bonding to Hybrid Materials

Due to their relative novelty, bonding protocols and surface pretreatment suggestions for hybrid materials have been difficult to find in the dental literature. Through the end of 2014, no independent scientific evidence pertaining to proper bonding protocols for new ceramic/polymer materials were available. Recently, a few in vitro studies have been published on this topic.[44-47] Studies by Elsaka,[44] Frankenberger et al,[45] and Peumans et al[47] tested the effect of different surface treatment methods on the bond strength of VITA ENAMIC and Lava Ultimate. Hybrid materials were tested with self-adhesive and self-etching composite cements in the studies.

Hybrid Ceramic

For VITA ENAMIC, all currently available in vitro studies found HF acid etching in combination with silane to be a superior pretreatment.[44-47] The application of HF acid partially dissolves the glass phase of VITA ENAMIC and provides undercuts in the micrometer scale for better micromechanical interlocking with a composite cement. Furthermore, the study by Elsaka[44] stated, in contrast to all other studies, that both HF acid and sandblasting followed by silane are reasonable surface treatments for use with VITA ENAMIC. However, the recently published working instruction of the International Academy for Adhesive Dentistry (IAAD) confirms the finding of the other laboratory studies and recommends pretreatment via HF acid etching and application of a silane.[48] The silica-based ceramic part of the hybrid ceramic seems to determine the best choice of surface pretreatment.

CAD/CAM Composite Resins

The studies confirmed, as it is recommended by the manufacturer, that Lava Ultimate should be subjected to air-particle abrasion and application of a universal bonding agent. High bond strength values were detected by Elsaka[44] and Peumans et al[47] when Lava Ultimate was pretreated with HF acid. This conflicts with both the findings of the Frankenberger[45] study and the manufacturer's guidelines.

To date, no scientific studies pertaining to the bond strength or the suggested adhesive cementation of CERASMART and SHOFU

TABLE 1

Overview of Hybrid Materials, Compositions, and Recommended Pretreatment Methods

CAD/CAM MATERIAL	MANUFACTURER	CLASSIFICATION	COMPOSITION	SURFACE TREATMENT	ADHESIVE SYSTEM
VITA ENAMIC	VITA Zahnfabrik	Hybrid ceramic	Aluminum oxide-enriched, fine-structure feldspar matrix (86 wt%, 75 vol%) infused by a polymer material consisting of UDMA and TEGDMA (14 wt%, 25 vol%)	60-second etching with 5% HF	Silane + composite cement
Lava Ultimate	3M ESPE	Resin nanoceramic	Bis-GMA, UDMA, Bis-EMA, TEGDMA, silica zirconia, aggregated silica/zirconia cluster	Air-particle abrasion with 50 µm Al_2O_3 (at 2 bar)	Ceramic primer (silane) + composite cement
SHOFU Block/Disk HC	Shofu	CAD/CAM ceramic-based restorative	Silica powder, zirconium silicate, UDMA, TEGDMA, micro-fumed silica, pigments, and others	Air-particle abrasion with 50 µm Al_2O_3 at 0.2 - 0.3 bar for 10s)	Ceramic primer + composite cement
CERASMART	GC America	Flexible nanoceramic	Silica, barium glass, Bis-MEPP, UDMA, DMA	Air-particle abrasion with 50 µm Al_2O_3 at 1.5 bar)	Ceramic primer (silane) + composite cement

Abbreviations: Bis-GMA = bisphenol A glycol dimethacrylate, Bis-EMA = ethoxylated bisphenol A glycol dimethacrylate, Bis-MEPP = bisphenol A ethoxylate dimethacrylate, DMA = dimethacrylate, TEGDMA = tetraethyleneglycol dimethacrylate, UDMA = urethane dimethacrylate.

HC are available. However, due to their similar compositions, similar recommendations for their adhesive placement can be made for Lava Ultimate. As it is suggested by manufacturer, both materials should be pretreated through air-particle abrasion and application of a universal bonding agent.[39,49]

Furthermore, the IAAD advises pretreatment for CAD/CAM composite resins with either air abrasion of 50 µm of aluminum oxide or 30 µm of silicon oxide at a pressure of 2 bar.[50] This leads to the conclusion that surface treatment via air-particle abrasion appears to be the best choice for CAD/CAM composites.

Table 1 gives an overview of the currently available hybrid materials, their compositions, and recommended pretreatment methods.[31,37,39,40,45,49] A clinical case using a resin-bonded hybrid ceramic (VITA ENAMIC) is displayed in Figure 1 through Figure 16.

Conclusion and Clinical Recommendations

Based on the current scientific evidence, the following recommendations for clinical application and successful implementation of these new materials with promising mechanical properties can be drawn: (1) hybrid ceramics with a double interpenetrating network should be pretreated with HF acid and a silane coupling agent should be applied prior to cementation; (2) CAD/CAM composite resins with a resin matrix should be subjected to air-particle abrasion and application of a universal bonding agent; and (3) all hybrid materials should be luted adhesively with either light-curing or dual-curing resin cements. These recommendations notwithstanding, clinical studies are needed to evaluate the long-term bonding behavior and the survival rates for this new materials family.

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