The Proceedings of the 2011 Autumn Meeting of the EAED (Active Members' Meeting) – Versailles, October 20–22nd, 2011

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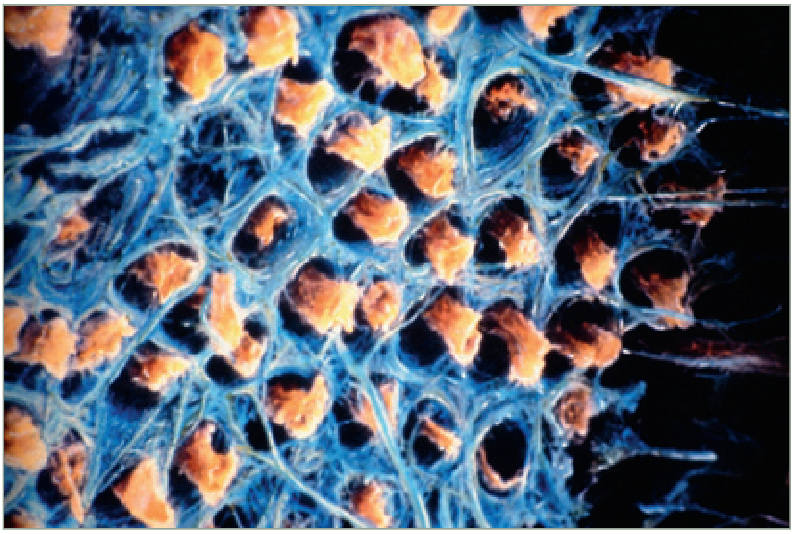

SEM image of a section of occlusal dentin 1 mm far from the pulp. The dentinal tubules and the odontoblastic process are visible (courtesy of Vassilios Kaitsas/Luciano Fonzi).

Material interfaces in Esthetic Dentistry

Prologue of the Scientific Chairman

One of the major scopes of the EAED is "to provide leadership in the profession by defining the highest ethical standards and to foster interdisciplinary communication and research through publications and educational presentations."

In the pursuit of esthetics within the human body, the issues of beauty, health and integrity ought to be found in a non-disrupted link. In Esthetic Dentistry, heterogeneous substances ought to come into a long lasting synergy and conduct the realization of the ultimate integral response of an esthetic outcome. Thus, in restoring the mutilated dentition, the material interfaces act as a most delicate link in composing a clinical intervention of harmony. A clear documentation, definition and demonstration of the limits in applying the materials and executing the procedures at a level of clinical excellence through an interdisciplinary official communication is still academically missing.

The Versailles workshop was structured under the general theme: "Material Interfaces in Esthetic Dentistry." The presented essays addressing specific issues were prepared well in advance, all containing cutting-edge experimental evidence information of the material science, and the relevant clinical interpretation and were communicated to all participants beforehand. The interactive and comprehensive discussion that followed the presentations was recorded, and after careful editing and accurate evaluation, conclusions were drawn. Thus, from the proceedings of the meeting the present document was developed, the publication of which intends to become of help for all readers – clinicians or researchers.

At this point, it is more than appropriate for the Scientific Chairman of this meeting to extend his genuine gratitude to the three Essayists, Prof Angelo Putignano, Prof Markus Blatz and Prof George Eliades and to the two Moderators, Prof Vassilios Kaitsas and Dr Stefano Gracis for their willingness to invest their hard work and precious time for the success of such a demanding workshop, which was structured as follows:

- Part I – Adhesion On Dental Substrates
- Part II – Cementing, Supporting and Veneering Prosthetic Dental Materials.

Part I – Adhesion On Dental Substrates

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Essayists:
Clinical Parameters:
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Experimental Evidence:
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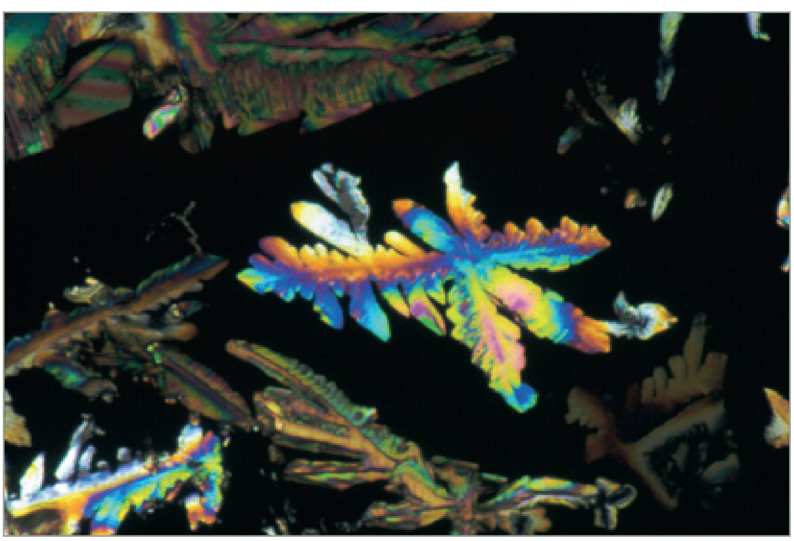
Discussion:
Vassilios Kaitsas and **Aris Petros Tripodakis**



Polarized light image of the early stages of gelation of maleic acid with 2-HEMA (courtesy of George Eliades).

Introduction

by the Moderator,
Prof Vassilios Kaitsas

In restoring lost dental tissues, the adoption of adhesive procedures is very frequent. Resin composite adhesion, common for small fillings, aims today to embrace the full spectrum of restorative dentistry that is provided even for the severely mutilated dentition. The success of any adhesive procedure is tied together with the meticulous analysis of all factors involved, related to the nature of the restorative material and the recipient tooth surface. Fundamental parameters for choosing the kind of material, which will be used relative to the restorative procedure, depend on the different chemical and structural composition of the dental substrates and the chemical composition of the material itself.

The typical structure of dentin contains 70% (wt) hydroxyapatite, 12% water and 18% organic components (collagenic fibrils, proteoglycanes, dentinal fluid, cells, etc). However, deep carious lesions in young patients contain increased percentage of hydroxyapatite (sclerotic dentin). In other situations, dentin can be found with more or less organic components, as for example, when irrigated with sodium hypochlorite during root canal treatment or crown dentin after a bleaching procedure. In all of these different cases and some others, the indiscriminate use of any enamel-dentin adhesive system available on the market is not indicated (Figs 1 to 9).

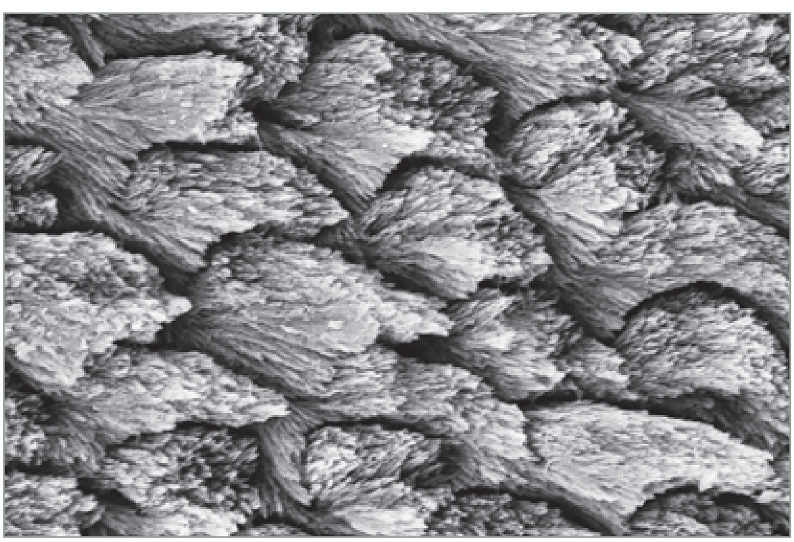


Fig 1 SEM image of unetched enamel.

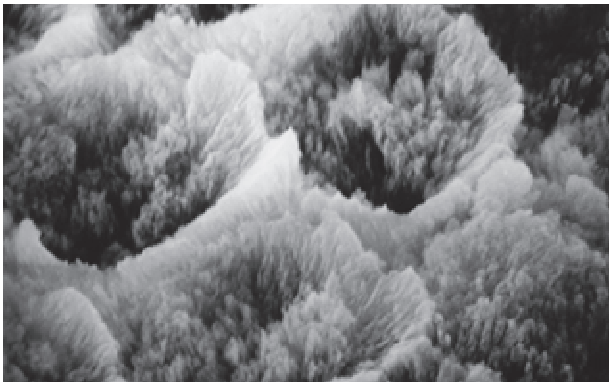


Fig 2 SEM image of etched enamel with phosphoric acid 37% for 30 sec.

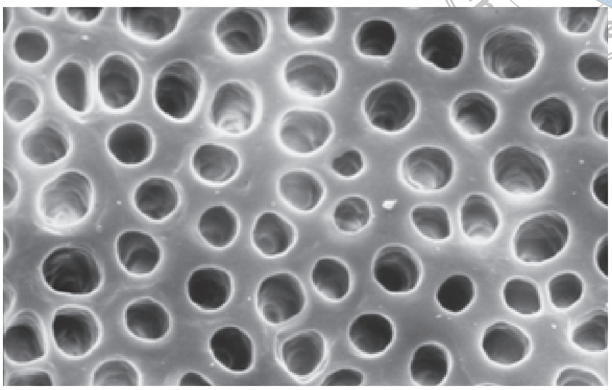


Fig 3 SEM image of etched dentin with phosphoric acid 37% for 15 sec.

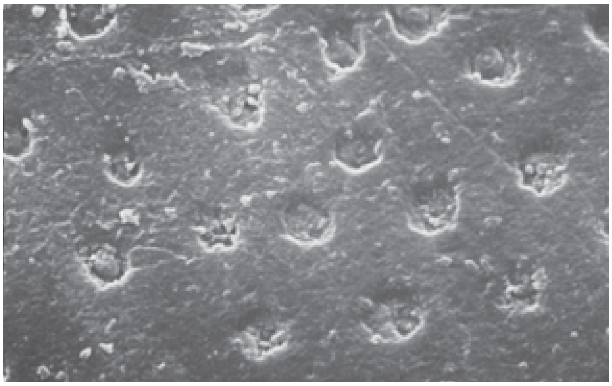


Fig 4 SEM image of sclerotic dentin at cervical crown third.

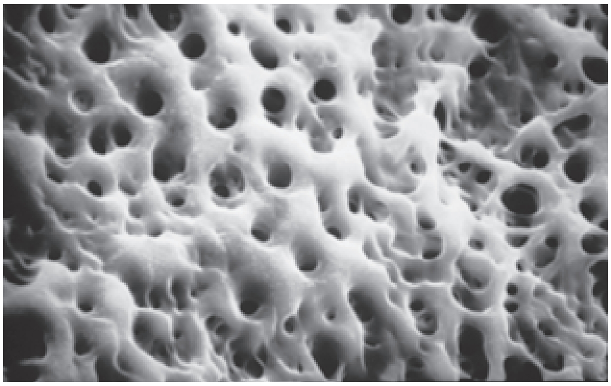


Fig 5 SEM image of a section of dentin 1 mm far from the pulp at a cervical area. The dentinal tubules are visible.

In general, the more chemical reactions are involved with the substrate, the better the adhesion will be. Some of the adhesive systems are formulated to obtain chemical links with specific ions of the enamel and/or dentin. For example, phosphoric esters of Bis-GMA of some of the commercial products react with the calcium ions of the hydroxyapatite of enamel or dentin. Some other adhesive systems which are made with chemical groups containing nitrogen, react with similar groups of the organic part of dentin, especially collagen.

Very often the quantity of the available enamel is limited. In these cases, both the correct etching procedure in combination with an appropriate adhesive enamel-dentin bonding system assure the success. Consequently the choice in applying a specific self-adhesive resin material with or without the use of a self-adhesive bonding system complicates the clinical decision-making. Such dif-

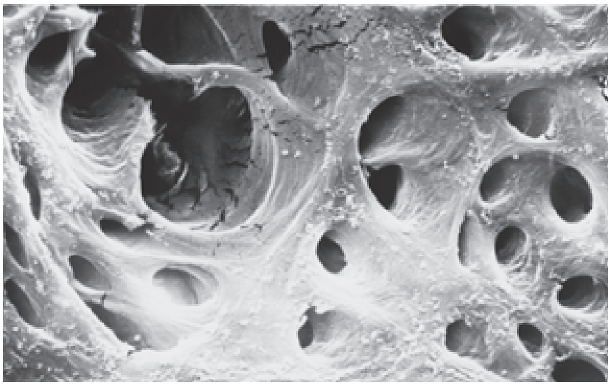


Fig 6 SEM image of cervical dentin very close to the pulp.

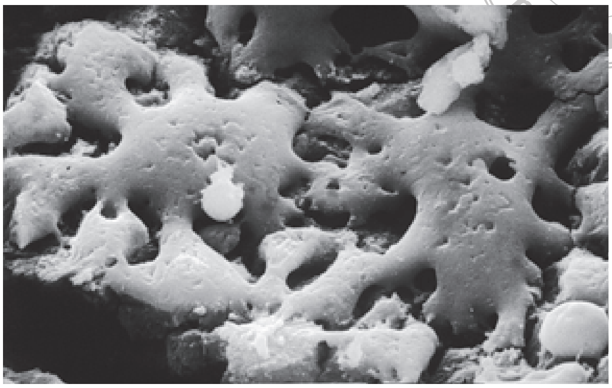


Fig 7 SEM image of dentin section after Nd:YAG: laser treatment (without water, 5 x 20 exposure).

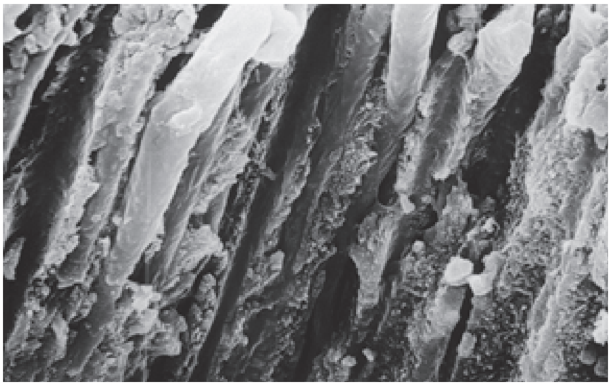


Fig 8 SEM image of dentinal tubules filled with an endodontic sealer.

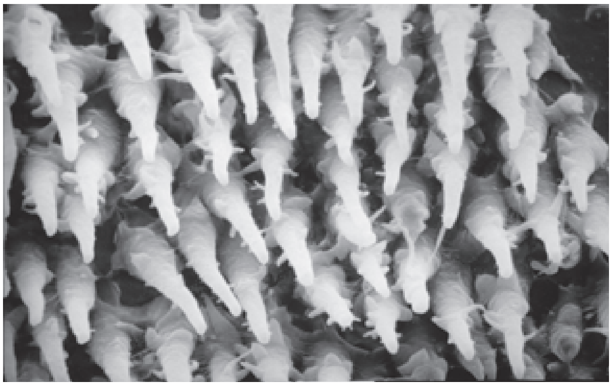


Fig 9 SEM image of resin tags extending into dentinal tubules. Cervical section of a root canal treated tooth after adhesive treatment for fiber post luting.

ficulties are even more often faced when cementing a prosthetic crown, a laminate veneer or a post in a root.

In the light of recent research evidence, the pursuit of excellence should be founded on its clinical interpretation and execution. The essayists will try to explain the concepts and operation precautions that should be considered in dealing with adhesive procedures.

Their essays will address the following issues:

- Do clinical steps and timing influence the quality of adhesion?
- Are different adhesive systems needed for different dental and restorative substrates?
- Are different adhesive systems needed for different restorative procedures?

The Essays

Clinical Interpretation of the Scientific Evidence on Adhesion on Dental Substrates

Essayist, Prof Angelo Putignano

Introduction

The outcome and the stability of dental adhesive restorations are dependent on the materials, dental substrates, patient-related factors and clinical steps used by a clinician.[1-3] External factors – such as the skills of the operator, isolation method, timing of etching and adhesive application, type of light source, finishing instruments used, etc – significantly influence the outcome.[4] Therefore, appropriate protocols for the clinical use of different adhesive systems have to be followed. Dental adhesives can be classified according to: a) their action – either removing the smear layer (etch-and-rinse technique) or maintaining it as the substrate for bonding (etch-and-dry or self-etch technique), and b) the number of clinical steps.[3]

The purpose of the present report will be to briefly discuss the following issues:

- Do clinical steps and timing influence quality of adhesion?
- Are different adhesive systems needed for different dental and restorative substrates?
- Are different adhesive systems needed for different restorative procedures?

Essay 1a: Clinical steps and timing in adhesion

In the three-step etch-and-rinse technique, which remains the golden standard, the kit may contain a dual-cure option for indirect restorations. Thus, the multiple bottles can make their utilization cumbersome and the sequential application of the primer and adhesive resin may be inverted. The protocol should include: etching for 15/30 s enamel, 15 s dentin, extensive rinsing for the same amount of time; application of 2–3 layers of primer – air; bonding application – air and light-curing (between 20 and 40 sec, depending on the type of light-curing units).[5]

The two-step etch-and-rinse-technique makes the one-bottle concept extremely user friendly; however attention must be paid regarding the respective adhesive solvent. For instance, acetone-based adhesives may lose their efficacy with constant usage and may need more coats than those recommended by the manufacturer.[6]

The etch-and-dry (or self-etch) technique can include either two- or one-step systems, depending on whether the etching/primer agent is separated from the adhesive or combined with it to allow a single application. The multi-bottle system may offer the advantages of no rinsing and quick application. It is important to respect the application time of the acidic primer and the bonding before polymerization; it may not be effective on sclerotic dentin and may result in enamel microleakage, due to deficient enamel etching (enamel pretreatment can be suggested as an additional clinical step).[5]

The all-in-one application may be a very quick alternative, but has resulted in a wide range of bond strength values, needs multiple coatings to bond effectively to dentin and has not proven its efficacy over time.[5] The use of the one-bottle adhesives showed a typical chemical degradation of the oxygen-inhibition layer at the border between the adhesive and the resin composite, that may reduce the long-term stability of resin–dentin bonds.[2]

Recently, pre-etching and newly formulated one-step self-etch adhesives have demonstrated an increased bonding both on dentin and enamel.[7] Among self-etch adhesives, mild self-etch systems have the advantage to keep some hydroxyapatite crystals around collagen fibers, thus protecting the collagen against hydrolysis and early degradation of the bond.[8]

Interpretation in clinical application

Causes of failure for the etch-and-rinse techniques may be: over-etching, incorrect sequence, or multi-layering. On the other hand, in the self-etch technique (especially in the "all-in-one application") failures can be due to: loss of stability over time, phase separation, low degree of conversion, or continuous etching.[5] A concern is the effect of residual water that remains within the adhesive interface, which cannot be completely removed. Some self-etch agents present only water as a solvent. However, in many systems, the water is associated to ethanol, acetone or even to monomer. Special attention should be directed to water-based agents, mainly the all-in-one agents. A multiple layer application under a continuous brushing technique has also been claimed to increase the bond strength of these materials.[9] On the other hand, as water has been related to phase-separation, polymerization inhibition and reduced shelf-life, the development of self-etch water-free adhesive has already been proposed.[10,11] The water necessary to trigger the acidic reactions would come from the dental substrate. Another simple approach to improve bonding is a mild air-blowing of the adhesive which might help to remove interfacial water, thus improving bonding effectiveness.[12]

There are various clinical procedures that have been proposed to be effective in optimizing bonding and reducing bonding degradation after aging – such as extended polymerization time,[13] improved impregnation (ie, prolonged application time), use of a hydrophobic coating to reduce water sorption and stabilize hybrid layer, and use of inhibitors of metallo-proteinases (MMPs), which are the enzymes responsible for the bonding degradation.[5]

Essay 2a: Different adhesive systems for different dental and restorative substrates

The ultimate goal of a bonded restoration is to attain an intimate adaptation of the restorative material with the dental substrates (enamel, dentin, etc) and the different restorative substrates (resin composites, conventional ceramics, non-silica based ceramics).

While adhesion to enamel is stable over time, adhesion to dentin is more unstable, because of its heterogeneous characteristics.[14] The wetness of dentin surfaces, the presence of pulpal pressure, and the thickness of dentin are extremely important variables during bonding procedures, especially when testing bond strength of adhesive materials *in vitro* with the intention of simulating *in vivo* conditions. While enamel is predominantly mineral, dentin contains a significant amount of water and organic material, mainly type I collagen.[15,16] Several other substrate-related variables may affect the clinical outcome of bonded restorations.

In general, higher bond strength values were obtained for permanent dentin than for dentin of primary teeth, in which total-etch adhesives displayed higher shear bond strength values than the self-etch adhesives.[16]

Bonding to caries-affected dentin is hampered by its lower hardness, presence of mineral deposits in the tubules and disorganized collagen.[17] Hybrid layers in caries-affected dentin are usually thicker but more porous than those in sound dentin.[18] Non-carious cervical areas contain hyper-mineralized dentin and denatured collagen, which is not the ideal combination for a bonding substrate. Physiological transparent root dentin that forms as a natural part of aging, is similar to the transparent dentin observed underneath caries lesions with the tubule lumina filled with minerals, which makes resin hybridization difficult.[19]

An increase in number of tubules with depth and, consequently, increase in dentin wetness, make bonding to deeper dentin more difficult than to superficial dentin. Dentin permeability increases with cavity depth and acids that remove the smear layer can also increase it. Etch-and-rinse adhesives result in higher micro-permeability compared to self-etch ones.[20] The application of acidic agents open the pathway for the diffusion of monomers into the collagen network; it also facilitates the outward seepage of tubular fluid from the pulp to the dentin surface, deteriorating the bonding for some of the current adhesives.

Further factors that might influence the bonding efficacy are: the orientation of the dentinal tubules and other regional variables, and the instruments used to create the smear layer. For instance, dentin surfaces ground with diamond burs tended to present compact smear layers with a density that may compromise bonding action, especially with self-etch systems.[21]

Figures 10 to 12 show different substrates in anterior teeth and the final successful result that could be obtained. Successful anterior restorations can also be manufactured when the dental substrates are not “ideal” (Fig 13). Substrate variables can be observed in posterior teeth as well (Fig 14).

All these substrate variables, as well as the deterioration of the bonding observed over time, have to be taken into account while choosing bonding strategies. A new approach to stop the degradation of dentin-resin interfaces is the use of MMP inhibitors, such as chlorexidine.[22,23] Indeed, the use of very low concentrations of chlorexidine after phosphoric acid-etching inhibits MMPs activity, thus preserving aged dentin-resin interfaces.[19] Although still in an

Fig 10 Ideal dental substrates in anteriors: preparation for ceramic veneers only in enamel.

Fig 11 No ideal dental substrates in anteriors: composites, dentin, caries-affected dentin, cement.

Fig 12 Preoperative view of a case without an expected sufficient adhesive outcome.

Fig 13 Postoperative view of the final successful case.

Fig 14 Different dental substrates in posteriors.

early phase of *in vitro* and clinical research, this method seems promising.

Clinical interpretation

While adhesion to resin composites is stable over time, adhesion on other restorative materials is less stable, because of their different characteristics. Bonding to traditional silica-based ceramics, generally employing both mechanical and adhesive retentions, has been well researched and bond strengths are predictable.

A strong resin bond relies on chemical adhesion between the cement and ceramic (by way of silane chemistry), and on the micromechanical interlocking created by surface roughening. Current roughening techniques are: (1) grinding, (2) abrasion with diamond or other rotary instruments, (3) air abrasion with alumina or other particles, (4) acid etching (typically hydrofluoric acid, or HF), and (5) a combination of any of these techniques. Unfortunately, the composition and physical properties of certain materials like zirconia differ from conventional silica-based materials, and require very aggressive mechanical abrasion methods to increase surface roughness, possibly creating strength-reducing surface flaws.[24] Therefore, in order to achieve acceptable cementation in a wide range of clinical applications, alternate attachment methods, ideally utilizing chemical adhesion in addition to mechanical retention, are required.

Essay 3a: Adhesive systems and different restorative procedures

Different restorative procedures may need different types of bonding systems. Literature reports generally differentiate adhesive approaches for direct versus indirect restorations.

The *in vivo* adhesives performance for direct restorations is mainly studied by means of clinical trials on class V restorations. A recent review[25] searched all studies between 1998 and 2004, on the clinical effectiveness of different adhesive systems in Class V restorations. The observation period of the studies varied between 0.5 years and 6 years. Three-step etch-and-rinse adhesive systems and 2-step self-etch adhesive systems showed a clinically reliable and predictably good clinical performance, with a mean annual retention loss of 4.8% and 4.7% respectively, whereas the mean annual retention loss of 2-step etch-and-rinse adhesive systems was 6.2%, and that of 1-step self-etching adhesives 8.1%. Another recent review[26] reported the studies conducted at the Catholic University of Leuven. Retention rate of class V restorations up to 13 years for the three step etch-and-rinse adhesives was recorded from 94% to 84%. Retention up to 8 years for 2-step self-etch adhesives was about 97%. Retention up to 3 years for 1-step self-etch was recorded in a range between 98% and 94%.[26]

The “all-in-one application” is generally not indicated for indirect restorations. Nowadays, however, some adhesives of the 1-step self-etch group (with phosphoric acid pre-treatment) have also demonstrated a high value of bonding when applied in dentin and enamel.[7] *Luting indirect restorations:* If margins are in enamel, the etch-and rinse adhesives and the etch-and-dry systems with pre-etching treatment performed well. When margin are in dentin, the total-etch technique with a 3-steps etch and-rinse is still considered the gold standard.[26] The final film thickness of a resin adhesive and a resin cement could be affected by previous polymerization of the adhesive systems on dentin surfaces. Instructions regarding polymerization of the adhesive layer must be followed when adhesive systems are used in combination with dual polymerized resin based cements.[27]

Clinical application

In case of inlays, onlays and overlays, the following uses can be suggested: (1) a 2-step self etch adhesive to make the build-up and to treat the dentin on the day of inlay preparation; (2) a total-etch adhesive (preferably a simplified system, which can be polymerized because of its low thickness of 10–20 μm) on the day of inlay cementation.

In the case of luting ceramic veneers with margins on enamel, the total-etch technique can be suggested, using simplified (low-thickness and low-viscosity) bonding systems. Translucency and opacity of the veneers have also to be taken into account. For instance, when the veneer is opaque, it is advisable to treat the prepared tooth by applying and light-curing a simplified adhesive. On the other hand, when the veneer is translucent, the adhesive can be left uncured and a 3-step system can be used.

Low-viscosity and extremely thin bonding agents are recommended for porcelain veneers and inlays because they do not compromise the fit (preferably polymerized before placing the restorations). High-viscosity (high filler content) bonding systems can be effective for replacing old restorations with sclerotic dentin, or in case of slow caries-affected regions.

Final considerations

Several research lines have been proposed and investigated in the past years regarding the relationship between laboratory tests and clinical outcomes of dentin adhesives. As can be noted by the issues discussed in this short report, keeping an updated knowledge of the mechanisms of adhesion, characteristics and timing of the currently available adhesive systems, as well as knowing how the dental and restorative substrates interact with these materials, are essential for achieving the best results in adhesion. Reasonable correlation was found between some aged bond-strength laboratory data and 5-year clinical data.[26] Therefore, measuring the "aged" bond-strength should be encouraged to predict the clinical effectiveness of adhesives. Moreover, recent results have recently proposed the notion of "guided tissue remineralization" in order to obtain remineralization or crystallization within resin-dentin bonds after long-term function either *in vivo* and *in vitro*, using Portland cement and simulated body fluid.[28,29]

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Experimental Evidence On Adhesion On Dental Substrates

Essayist: Prof George Eliades

Introduction

Bonding of restorative materials to dental hard tissues has long been recognized to be of paramount importance for the strength and durability of restorative treatments. Currently, with the rapid development of dimethacrylate-based dental restorative materials, a variety of adhesive systems have been introduced, that are usually classified based on the conditioning mode of the tissues (etch and rinse/self-etch) and the clinical steps involved (3-, 2-, 1-step).[1] All these procedures aim to (a) remove, dissolve or modify the smear-layer produced during cutting, and (b) infiltrate the etched enamel structure, the mineral-depleted collagen of intertubular dentin, and tubule orifices with in situ polymerizable resin monomers.[1,2]

Essay 1b: Steps and timing in adhesion

Three-step etch and rinse adhesives are still considered as the "gold standard," based on their documented laboratory and clinical performance.[1] Studies on the bonding mechanism of these adhesives revealed a bioengineered tissue augmentation by forming interdiffusion zones (the so-called hybrid zones) between acid-demineralized hard tissues and amphiphilic resin monomers.[1,2] These monomers are tailored to bridge the hydrophilic tissue characteristics with the hydrophobic nature of bonding resins placed onto it, to establish a surface compatible with the hydrophobic composite restorative materials.

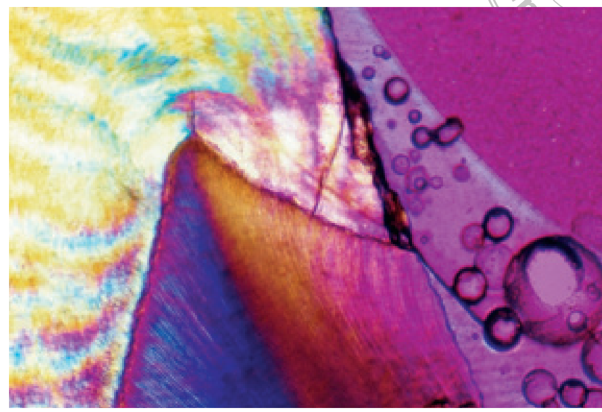

Fig 15 Longitudinal tooth section restored with the etch and rinse technique viewed under polarized light. Note the excessive porosity.

The three well-defined application steps were considered, mainly by marketing professionals, as being time consuming or prone to handling errors; hence, new products have been developed to speed up chairside time. Two-step etch and rinse adhesives, by mixing amphiphilic and hydrophobic monomers plus solvents (acetone, ethanol, water, isopropyl- or butyl-alcohol) to mediate monomer immiscibility in a single bottle, were then introduced. With these systems, though, various aspects of technique sensitivity were deployed, that were dependent on the type of solvent, including inadequate resin penetration down to the remineralization front, monomer phase separation and differential diffusion, need of bonding to hydrated tissues to avoid collagen collapse and shrinking (mainly for products with acetone), while avoiding overwetting, entrapment of residual solvent and polymer plasticization, reduced pot-life due to acid catalyzed monomer hydrolysis and incompatibility with slow setting materials (dual- or chemically-cured), due to formation of an acidic oxygen inhibited layer (Fig 15).[1,3-9] Moreover, the absence of a hydrophobic bonding resin layer and the increased dentin permeability due to acid-etching, established semi-permeable interfaces to tissue fluids, creating leakage within the hybrid zone (nanoleakage) and tissue-material interface (microleakage) vulnerable to hydrolytic and enzymatic degradation.[10] All these were clinically expressed by postoperative sensitivity and marginal adaptation problems.[11,12] However, it has been recently postulated that ethanol-wet bonding may diminish many of these drawbacks.[13]

A more efficient approach of bonding to dentin was the use of the 2-step self-etch adhesives, where phosphoric acid etching is replaced by a non-rinse acidic monomer treatment, plus a separate hydrophobic bonding resin layer. This approach overwhelmed the limitations of the previous adhesives, especially when mild acidic monomers were introduced (pH~2) that, instead of demineralizing, bonded or chemisorbed onto dentin mineral, thus establishing a more durable interface.[14] Nevertheless, the main problem of these adhesives was the limited shelf-life, due to acidic monomer hydrolysis[8] and the limited capacity of durable bonding to enamel.

To improve performance, amphiphilic methacrylate ethers instead of esters have been introduced and a separate step of enamel acid-etching has been advocated, actually transforming these systems to 3-step systems. Single-step adhesives (mix or no-mix), considered as the latest and most advanced development in the field, suffer from the same problems of 2-step etch and rinse adhesives plus inadequate bonding to enamel.[14] The latter can be addressed by the addition of a separate acid-etching step.

Based on the history of the adhesives development and the current knowledge on tissue hybridization mechanisms, it seems that the most effective adhesive should include enamel acid-etching with phosphoric acid, dentin treatment with a mild acidic amphiphilic monomer and a topcoat of a bonding resin, free of acidic monomers, that points back to the early 1990s when such systems were available.

Essay 2b: Adhesives and the dental substrate

The type of the dental substrate plays a fundamental role in the performance of an adhesive system. Although most modern adhesives are marketed as universal adhesives, there are great variations in their performance on different hard tissue qualities and restorative materials.

Typically, most laboratory studies involve evaluation of bonding properties with intact tissue. However, the structural heterogeneity greatly affects strength. For example, when bonding to prismless, hypomineralized and hypoplastic enamel, it is much lower than normal.[15,16] On sound dentin, micro-testing systems revealed that the interfacial strength depends on tubule orientation (cross- or longitudinal sections) and in-depth locations (differences in mineral content); (Fig 16).[16,17]

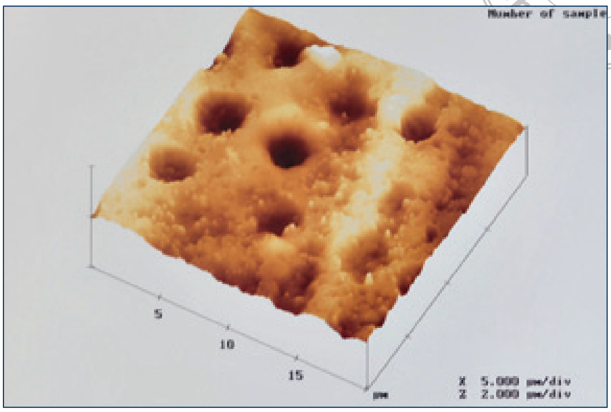

Fig 16 Collagen swelling of a phosphoric acid-etched dentin after primer treatment. (Tapping mode Atomic Force Microscopy image).

Pathological dentin demonstrates a wide range of bond strength values, always lower that intact tissue. Caries-affected dentin, being structurally disorganized, results in low bond strength, with wide, porous and atypical hybrid zones, regardless of the adhesive used. Caries-infected dentin exhibits a non-universal hybridization pattern.[16] For this substrate, self-etch contact-disinfecting adhesives have been advocated. However, the extent of collagen depletion plays a crucial role in the treatment outcome. Problems of low bond strength also arise with hypomineralized dentin.

NaOCl conditioning may increase the mineral to collagen ratio in such cases, but this treatment should be followed by antioxidant post-conditioning (ie, sodium ascorbate, glutathione) to neutralize the deproteinating capacity of residual NaOCl.[18] The same procedure has been advised for hypoplastic enamel as well.[19] Mild self-etch adhesives are considered as the best restorative approach for such cases, to avoid excessive depletion of residual mineral from the affected tissue. Hypermineralized tissues require aggressive adhesive treatments (pH <1) to expose normal structure, if possible, or mechanical removal of the superficial sclerotic layer (Fig 4).[20,21] Bonding to freshly bleached enamel and dentin is another difficult task, due to residual oxidative radicals. Treatment with antioxidants seems to offer a viable alternative.[22,23] Bonding to lased dentin is quite challenging.

For Er:YAG laser treatments, it has been found that subsurface dentin, up to a depth of 3-5 µm, is modified exhibiting a dense but fissured layer with a limited amount of denatured collagen at the transitional area with intact dentin, leading to low bond strength (Fig 7). On such substrates, mechanical removal of this zone or conventional acid-etching may restore bond strength.[1]

Bonding to root canal walls is a quite complex task due to variations in dentin structure, composition and topography that makes several treatment steps of limited effectiveness (Fig 8).

The stability of the adhesive systems and their interfaces over time has been the subject of many studies. In several 1-step products, acidic methacrylate esters have been replaced by acidic ethers, to avoid acid catalyzed ester hydrolysis as in other adhesives as well.[8,24] Enzymatic degradation of collagen, mainly by metalloproteinases, has been considered as important for the long term interfacial stability.[25,26] However, in the light of new evidence, it seems that this procedure may affect mainly fully exposed collagen, giving credit to treatments that includes mild demineralization agents.[27]

Finally, there are still efforts to probe whether a primary bond can be formed between adhesives and dentin, either via mineral or collagen, since a molecular bonded interface is energetically more stable. For modern materials, there are sporadic data probing calcium phosphate or calcium carboxylate intermediates on treated dentin surfaces and mainly secondary bonding with collagen, the latter being of much lower reactivity to form primary bonds.[2,14]

Essay 2c: Adhesive systems and restorative procedures

A plethora of laboratory studies have been performed to investigate the effect of a variety of parameters mainly on tooth restorations to simulate the clinical conditions. Internal and marginal adaptation tests have shown that the efficacy of the adhesives is dependent on the flexural modulus of the restorative composite.[1] For direct restorations, the film forming properties (setting capacity and strength, extent of oxygen inhibition, rheological characteristics and surface tension) are considered to be of primary importance. Non-uniform film thickness, total inhibition of setting, porosity, wrinkling and debonding are some of the defects related to adhesive application and exposure to composite setting shrinkage.[3] Marginal adaptation is generally better when acid-etched enamel margins exist.[28]

The use of flowable liners may improve adaptation, provided that the liner, upon co-polymerization with bulk resin, can efficiently buffer composite setting shrinkage forces. When calcium hydroxide bases or liners are used (the efficacy of which have been put in question), acidic primers should not be placed in direct contact with the former. An intermediate layer of glass-ionomer may protect the calcium hydroxide liner, although still part of it may be neutralized. For composite core build-ups, adhesives should be used along with dual-cure activators, especially when acidic monomers are employed, which deactivate the amine components of the chemically curing mechanism.[29]

For indirect restorations (inlays, onlays), minimal adhesive film thickness is required when light-cured materials are used and polymerized before inlay placement. However, this procedure may result in totally inhibited film thickness by oxygen, jeopardizing adhesion. Instead, dual cured versions are preferred. When using the 2-step "resin-seal dentin technique," during the first appointment, the entire surface of cut dentin is transformed into hydrophobic dentin, from the bonding resin applied onto. Therefore, the rationale of using acidic adhesives onto hydrophobic dentin during restoration luting is a matter of controversy.

For bonding to root canal dentin walls, 3-step or self-etch adhesives have been introduced, all with dual-curing capacity, to compensate for the strong attenuation of the activating light. For luting opaque ceramic veneers, dual-cure adhesives may be used as well. For transparent veneers, light-cured luting agents free of adhesive monomers are a good choice, due to the better color stability. Nevertheless, the light-cured adhesives used as a separate step, are not color stable and may affect the color of the final restoration, especially after aging.[30]

Finally, for bonding on dimethacrylate composites, surface treatment with MMA-dimethacrylate mixtures has been advocated to activate the substrate and promote graft copolymerization, although several concerns have been expressed on the role of MMA.[31] The latter is more effective when bonding to heat-cured methacrylates.[32]

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Discussion on adhesion on dental substrates

(Edited by Vassilios Kaitsas and Aris Petros Tripodakis)

Vassilios Kaitsas
To bond composite onlays and inlays, preheating the composite material to 45–50°C is often recommended. How can good polymerization be ensured for the composite cement beneath dental material and tissue, which absorb the energy provided by the normal photopolymerizing lamps used in dental practice?

Angelo Putignano
There are two things that ensure good polymerization. If the correct protocol is followed, the direct build-up that precedes the cementation confines the thickness of the indirect restoration to 2–2.5 mm. The second is to use very powerful polymerizing units, such as the EMS Master Light (EMS, Nyon, Switzerland), which provides up to 3,000 mw/cm^2, or the Ultradent Valo model (Ultradent, UT, USA) model, which provides 3,500 mw/cm^2. Normally, beneath 2 mm of composite, about 20% of the energy is absorbed on the surface; thus if the initial energy is over 3,000 mw/cm^2, a 20% loss would be less than 600 mw/cm^2, which is the energy required for the polymerization of 1 mm of composite material exposed to irradiation for 40 sec.

Vassilios Kaitsas
How is it possible to preserve the health of the pulp from the thermal insult that occurs during the conversion of monomers into polymers?

Angelo Putignano
I don't think that this problem arises because there is already protection with the build-up. In addition the temperature of the tip is about 50°C and on the tooth it does not exceed 35 to 38°C. It's also very difficult to determine the increase in the temperature of the pulp chamber for each individual case. Moreover, new high filled resin cements have less resin; thus when they polymerize, there is even less increase in temperature. For this reason, when an overlay must be cemented, it's better to use a resinous cement, whereas when cementing an inlay, it's better to use a material that is similar to the material used for the build-up or the inlay itself – that way you have the same degree of resistance to wear.

Vassilios Kaitsas
How different is it to treat dentin with or without dentinal fluid, for example, in the case of an endodontically treated tooth?

George Eliades
Reconstruction of a tooth crown is difficult, but it is even more difficult when the tooth has been subjected to root canal treatment. You need to humidify the tooth's structure. But this is only a minor part of the problem. There is a need to eliminate the eugenol residue when eugenol-based endodontic sealers have been used. In these cases, if you try to etch dentin with phosphoric acid for example, there is a reaction with the unstable zinc-eugenolate complex of the set cements, and free eugenol is released, which inhibits the polymerization of the resin components. Another question arises when attempting to create a "hybrid layer." In the crown dentin

it's possible to create this layer. However, in root dentin no one knows what actually happens, because of the different mineralization, tubule distribution and orientation, presence of residual endodontic material etc. Furthermore, some types of resinous luting agents used for post cementation polymerize very quickly in the absence of air, making it difficult to insert the post to the full length. To avoid this, it is recommended that the cement be "spread" on the post before inserting it into the canal. This, though, creates air voids after insertion. The self-adhesive luting systems with narrow and long application tips may provide valuable assistance to overcome these problems. In order to minimize the material interfaces, it has been advised to use dual-curing core build-up materials of medium viscosity as post luting-agents (with total etch or self-etch adhesives) and core built-up materials.

Vassilios Kaitsas

How stable is the pH of the various adhesive systems over time?

Angelo Putignano

To avoid the evaporation of the solvents normally contained in the adhesives (acetone, ethyl alcohol), single-dose components are recommended.

George Eliades

Three-step systems seem more stable, with distinct components per bottle. In systems containing non-functional hydrophobic and acidic hydrophilic monomers, the low pH destabilizes the ester groups through an acid catalyzed hydrolysis mechanism, resulting in degeneration and reduced pot stability and shelf life. Recent laboratory studies have shown that self-etching bonding systems with esters replaced by ethers are more stable and effective. Yet, this needs to be systematically confirmed over time.

Vassilios Kaitsas

To demonstrate how much better these products are, manufacturers often show us that the products have high resistance to debonding (30–40 MPa, which is excellent). Since this means good retention but not necessarily adhesiveness, could you provide us with evaluation criteria for the labyrinth of materials that are commercially available?

George Eliades

It's very difficult to clinically interpret the various experimental data reported in the manufacturers' leaflets. The clinical results can be scarcely predicted by the laboratory results. For example, even if the bond strength is high enough, this does not ensure good sealing. Microleakage may develop, leading to failure of the restoration. On the other hand, some materials have optimal sealing capacity on enamel and dentin, but low bond strength like glass-ionomers. Without a doubt, clinical documentation is the best predictor of the clinical performance. However, controlled clinical studies require a lot of time. Usually within this time frame, new materials are released in the market. This is the major reason why manufacturers provide laboratory results as the main means of product documentation.

Federico Ferraris

While the three-step adhesion is accepted as the gold standard, research data has shown that the best results for adhesiveness to the hard tissues of the tooth have been obtained using "etch and rinse" systems, followed by self-etching systems. What do all of you think about the benefits of using self-etching systems with few layers to apply, fewer errors to be made by the person performing the procedure, and lower postoperative dentin sensitivity? Are the fourth generation systems the winning choice?

Angelo Putignano

If you are very familiar with how a material is made and how it is used, it is possible to avoid complications. Mild self-etch systems are based on chemical bonding with the calcium ions of the enamel and the dentin. Generally, with one step self-etch systems the bonding has been demonstrated to be less stable than with the two-step self-etch systems. Indeed, the latter showed successful results, in Class V cavities, after 13 years, whereas long-term results of the one step self-etch systems are still under debate. When using the total-etch technique, there is a demineralization of about 10 µm. The infiltration depth with the adhesive systems is sometimes 6–7 µm and thus the 3 µm of not infiltrated dentin might be responsible for the postoperative sensitivity. If a meticulous protocol is followed, there are no complications, and this fact is true for both etch-and-rinse systems (the three-step and the simplified one-bottle systems). Personally I have used a single bottle etch-and-rinse system since 1994, and for 18 years I have had a 95% success rate. In accordance with the research of Costa and Pereira, the cavities that are only 0.5 mm from the pulp should be considered as being in contact with the pulp. For these reasons they suggest protecting the pulp with calcium hydroxide and glass ionomers before using adhesives. In all cases it's necessary to apply the etching agent for no more than 10 sec, which is rarely done, thus resulting in great postoperative sensitivity. On the other hand, when using self-etch systems, this hazard is avoided. The most accurate retrospective studies have been performed by the University of Leuven, which have reported results of adhesive durability from 6 months to 18 years.

George Eliades

Usually long-term clinical studies are limited to Class V cavities, because this is the ADA requirement. I would suggest enamel to be etched with orthophosphoric acid – all other alternatives are inferior. For dentin, it would be better to use mild self-etching systems; as you know, self-etch adhesives are classified in three groups according to their pH: strong, mild and weak. When we discuss this with regard to self-adhesive materials, it means that the material is placed directly into the cavity with no or minimal adhesive pretreatment (like a glass-ionomer filling). Recently some self-adhesive composite restorative materials have been introduced. The clinical performance of these materials is under evaluation.

Tidu Mankoo

Everything until now was very clear. To summarize, what do you recommend?

George Eliades

First etch the enamel with phosphoric acid, then use a mild self-etching adhesive material for the dentin and use a hydrophobic liquid resin, or the bonding resin provided by the 2-step self-etch systems. This brings us back to the older three-step adhesive systems. If you want to use a single-bottle adhesive system, it is better to “isolate” the adhesive layer with a topcoat of a conventional liquid resin (like Heliobond) to ensure that the hydrophobic character of the surface is left in contact with the composite. These procedures have been confirmed by a series of studies conducted by the group of Bart Van Meerbeek in Leuvain, which is considered among the world-experts in the field.

Tidu Mankoo
So you recommend the use of the “three step” adhesive systems?

George Elides
At least this has been proved clinically. Two-step self-etch systems are equally effective, but with an additional step of enamel etching with phosphoric acid.

Tidu Mankoo
Is there an advantage in utilizing an adhesive system with mild acidic primer, such as the self-etch Optibond FL (Kerr Dental, Orange CA, USA) or the original Scotchbond (3M ESPE, Berkshire, UK)?

Angelo Putignano
There is an advantage for the dentin because it is very gentle to the pulp, and the chemical adhesion is more stable.

Tidu Mankoo
Clinically how do you explain the success of some one bottle adhesive systems (like Scotchbond One), where with “etch and rinse” and with two layers of the adhesive liquid we observe a clinical success for about 20 years?

Angelo Putignano
The correct application protocol for the use assures us of the success.

Kony Meyenberg
I would like to ask the speakers their opinion about Optibond FL, which is not so popular but is used very often in various lab studies.

George Eliades
This is a typical three-step system with an additional particle-filled composite liner. The laboratory and the clinical performance of the system are ranked among the highest in the field. For this reason, it is used as a reference, especially in laboratory studies. Multistep systems may be further distinguished in two groups. Both groups need enamel acid-etching. In the first group, dentin is not acid-etched but is treated with a milder dentin primer, whereas in the second the acid-etchant is also applied on dentin, for less time (total-etch).

Didier Dietschi
The consistency and the composition of the etching gel can influence the final result. I would like to ask what kind of tests the manufacturers have to conduct to demonstrate the efficacy of their product?

Angelo Putignano
We have to keep in mind that the various adhesive systems are compared with the Optibond FL or other three or four similar systems like Scotchbond MP. So it’s enough to compare the laboratory data

of those two or three well known products with a new one. But other times, due to the fact that very often manufacturers pay for research, the resulting published data depends on the position of their product. If the study is on 20 products and the location is the 15th, they publish only the last five and their product becomes the first.

George Eliades

We should realize that the success of Optibond FL has been mainly established by clinical studies. For most of the materials, the bond strength is quite high for the first 24 hours, but over time there are variations, which may explain to a certain extent the differences observed in clinical studies.

Didier Dietschi

Which test is reliable for evaluating a new material?

George Eliades

The tensile/shear bond strength test and the micro-leakage test are required by ADA or EN specifications. There are a variety of tests available. In my opinion, fatigue tests by load cycling and hydrothermal-cycling are the most reliable, when the parameter of aging has to be addressed. Clinical trials are the ultimate test.

Didier Dietschi

How important is the micro-leakage test for the evaluation of a new material within the first hours?

Angelo Putignano

Today – and I don't know why – all the micro-leakage tests under a 2 mm thick composite layer of all products are negative!

Aris Petros Tripodakis

Angelo showed an indirect restoration with the interproximal margins on the direct composite build-up, and of course the hybrid layer created before taking the final impression. Is this the way to treat all the indirect restorations?

Angelo Putignano

In some cases, but not all. I prefer to do a direct restoration in the margin, and then to prepare the cavity and take the impression so placing the rubber dam for the cementation becomes easier.

Aris Petros Tripodakis

What about the rest of the preparation? Is everything sealed before taking the impression?

Angelo Putignano

Yes of course, I seal everything and I cure under glycerin two layers of bonding system, so we regenerate the bonding links to react with the cement. I think that the dual bonding technique is well known from the research findings of the Zurich school since 1997.

Vassilios Kaitsas

Also when we have to provisionally cement a temporary dental prosthesis with an eugenol cement like IRM, it is recommended the dentinal tubules are sealed and to control the integrity of the cement every two or three months.

John Orloff
I would like to ask about the mechanical preparation on enamel and on dentin prior to bonding.

Angelo Putignano
At the end of the cavity preparation, it is better to use a thin diamond or a multiblade bur to create a very smooth wall. This makes it possible to create a "uniform smear layer," which gives us better adhesion and more stable links especially when self-etch mild adhesive systems are used.

Silvia Jordao
I treated three teeth with a very conservative approach, sealing the root canals with resin-modified glass-ionomer resin and building-up the rest of the crown with multiple layers of resin composite, while the cusps were all intact. So I decided to leave them without further restoration. In a short time I had three failures due to mesiodistal fractures.

Angelo Putignano
The use of glass-ionomer material under the composite restorations is a mistake. It provokes the loss of the bond links between these two different materials, due to the higher expansion of the resin-modified glass-ionomer that probably caused the vertical fractures. The choice for such a conservative approach is the use of resin composite all the way.

Nitzan Fuhrer
George Eliades mentioned collagen stabilization with Gluma (Heraeus Kulzer, Hanau, Germany) or other chelating agents. How do you combine this approach with Optibond FL? Is the Gluma Primer itself good enough to stabilize the collagen?

George Eliades
In some situations it is. However, apart from glutaraldehyde, there are more contributors. EDTA helps chelate all mineral ions which otherwise may activate MMPs that destabilize collagen. Also, some primers, which contain polyacrylic acid like the Scotchbond MP Plus primer, may stabilize collagen by forming H-bonds. What came out recently at the last IADR/CED meeting was that it is not clear how MMPs affect collagen stability.

Nitzan Fuhrer
So you don't recommend the use of chlorexidine (CXE) before the use of the second bottle of Optibond FL?

George Eliades
The CXE role is rather puzzling. Collagen stabilization is necessary for the majority of the recently introduced adhesive systems. CXE if applied on dentin reacts with most sites available for he adhesive. Then what happens is not clear so far.

Nitzan Fuhrer
With my experience I used Consepsis (Ultradent, South Jordan, UT, USA) which contains 2% chlorexidine, to clean the cavity. I got a very bad pulp reaction and I was constricted having to do endodontic therapy. The concentration was probably very high.

Vassilios Kaitsas
From the study by Donovan that was published in 2009, it is clear that after 14 days the bond with dentin, treated with or without CXE, was similar.

Kony Meyenberg
Often in one abutment tooth, there is enamel, dentin and composite exposed. If silane is applied on the exposed composite, what would its effect be on the enamel and on the dentin?

Angelo Putignano
Silanes vaporize quickly in order not to negatively affect the bond. In the related literature, some papers favor the use of silanes in bonding procedures and others don't. Adhesion to ceramics is different. Some *in vitro* studies are in contrast with the clinical success. We need several clinical studies with the same protocol and the same evaluation criteria. But these random clinical studies are expensive for the manufacturers, and for that reason they only do laboratory *in vitro* studies.

Kony Meyenberg
I come back to my question: what happens if silane is applied on enamel and dentin after etching?

George Eliades
We have to understand what "silanization" means. There are two generations of silanes available in dentistry. The first one is a pure silane (or to be more correct silanol) that contains active hydroxyl groups for condensation and H-bonding, with traces of acidic acid to assist the production of silanols, an alkyl chain and a polymerizable methacrylate group. In the second group, acidic monomers, mostly phosphate with a structure similar to self-etch monomers, are used along with silanols. Both types may react with dentin creating a hydrophobic surface (similar to what is expected from a "hydrophilic" primer). Such an accidental contamination does not seem to create important problems.

Frederico Ferraris
During cementation of indirect restorations, curing the dentin bonding first has been suggested. What can be said about a different approach of curing the dentin bonding during the cementation phase?

Angelo Putignano
I prefer to obtain the hybridization of the dentin and cure the bonding system well, before taking the impression.

Vassilios Kaitsas
I ask George to tell us some advice about the self-etching resin cements?

George Eliades
These materials have some positive and some negative aspects. In the absence of light activation (as in the root canal) they convert slowly from the monomer state to polymer. At the same time, an acid-base reaction takes place to neutralize residual acidic groups with basic filler particles. The prolonged setting time and handling properties are in favor of the cementation or/ and post application procedures. Nevertheless, the low dark-curing conversion may create problems during early loading of the restorations. Inadequate curing may also be implicated with the long-term performance of the cements, including biological side effects.

Conclusions on adhesion on dental substrates

(by Vassilios Kaitsas and Aris Petros Tripodakis)

The following statements can be drawn from the presenters' lectures and the discussion that followed:

1. Clinical steps and timing in adhesion

1. In the three-step etch-and-rinse technique, which remains the gold standard in bonding, the protocol should include:
   a) Etching with phosphoric acid 32 to 37% concentration for 15 to 30 sec on enamel, 15 sec on dentin;
   b) Extensive rinsing for the same amount of time;
   c) Application of 2–3 layers of primer – air-dry;
   d) Bonding application followed by gentle air-blow;
   e) Light-curing for 20–40 sec (depending on the type of light-curing units).

2. The two-step "etch-and-rinse" technique makes the one-bottle concept appear to be user-friendly. However attention must be paid regarding the respective adhesive solvent that might require the application of more than one layer depending on its evaporability.
3. The "all-in-one" technique may also appear as a quick alternative. However the attained bond strength values have been found to be within an unpredictable wide range. It is not indicated on enamel and sclerotic dentin that would have to be etched separately.
4. Its effectiveness could be improved by the application of multiple coatings to bond on dentin, but it has not been proven durable over time, being affected by chemical degradation of the oxygen-inhibition layer at the interface between the adhesive and the resin of the composite.
5. The self-etch technique can also be applied by a two-step approach where the etching/primer agent is separated from the resin bond. It is important to respect the application time of the acidic primer, which might also require the application of multiple layers.

2. Different adhesive systems for different dental and restorative substrates

1. "Three-step" adhesive systems are generally effective and stable for bonding on enamel.
2. Prismless, hypomineralized and hypoplastic enamel should additionally be treated with hydrochloric acid and pumice prior to etching.
3. The adhesion on dentin in vital teeth is unstable because of its heterogeneous characteristics. The increase in number and width of tubules with depth, consequently increases dentinal wetness and makes bonding more difficult than on superficial dentin. The "self-etch" technique is indicated to seal freshly cut young dentin, especially in deep cavities and in dentinal hypersensitivity.

4. The application of acidic agents opens the pathway for the diffusion of monomers into the collagen network. To prevent this, the "self-etch" technique is indicated.
5. Dentin surfaces ground with diamond burs present a dense and compact smear layer that requires three-step total etch technique.
6. Laser-treated dentin has been found with a dense and occasionally fissured (depending on the laser wavelength) subsurface, up to a depth of 3-5 µm, with a limited amount of denatured collagen. On such a substrate, mechanical removal of this zone or conventional acid-etching assures adequate bond strength.
7. For bonding indirect restorations, a self-activator agent is additionally necessary in order to compensate for the strong attenuation of the activating light.
8. In non-vital teeth, for bonding to dentin and even more so on root canal walls, 3-step or self-etch adhesives have been introduced, all with dual-curing capacity.

3. Adhesive systems and different restorative procedures

1. In direct restorations, three-step "etch-and-rinse" adhesive systems and two-step "self-etch" adhesive systems showed a clinically reliable and predictable clinical performance.
2. The one-step self-etching adhesives are less stable. An intermediate layer of glass-ionomer may protect the calcium hydroxide liner when applied to deep cavities.
3. The "all-in-one" application is generally not indicated for indirect restorations. Nowadays, however, some adhesives of the one-step "self-etch" group (with phosphoric acid pretreatment) have also demonstrated a high value of bonding when applied to dentin and enamel.
4. In luting indirect restorations, if margins are in enamel, the etch-and rinse adhesives and the etch-and-dry systems with pre-etching treatment perform well.
5. When the margins are in dentin, the total-etch technique with a three-step "etch-and-rinse" procedure is still considered the gold standard.
6. Instructions regarding polymerization of the adhesive layer must be followed when adhesive systems are used in combination with dual polymerized resin based cements.
7. The use of flowable liners may improve the adaptation of the restoration on the margins, provided that the liner upon co-polymerization with bulk resin can efficiently buffer composite setting shrinkage forces.
8. For composite core build-ups, adhesives can be used along with dual-cure activators, especially when acidic monomers are employed, which deactivate the amine components of the chemically curing mechanism.
9. For luting opaque ceramic veneers, dual-cure adhesives may be used. For transparent veneers, light-cured luting agents free of adhesive monomers are the best choice.

Table 1 Clinical procedures for the cementation of fiber posts and composite indirect restorations.

What	Procedure	With what	On what
Glass fiber post (chosen according to the taper of the endodontic canal)	• Silanization (3 min at 60°C) bonding + • Light polymerization for 40 sec.	• Dual cured composite resin cement, OR • Self adhesive resin cement	Dentin: a) clean carefully endodontic materials b) etch for 30 sec c) wash + dry slowly + paper cones d) bonding + activator e) absorb the excess of the resin with paper cones.
Composite veneer, inlay or onlay	• Solvent (acetone- alcohol) • Air abrasion • Silanization (1 min at 60°C) • Bonding + light polymerization for 40 sec.	• Flowable composite, OR • The same type of composite, heated at 37°C for 3 min and polymerized for 90 sec, OR • Dual cured composite resin cement, and application of air block gel.	Enamel and sclerotic dentin: a) etch with H3PO4 for 30 sec b) wash and dry slowly c) bonding + light polymerization for 40 sec. Dentin: AS ABOVE, but etch for 15 sec or use a mild self-etch system two-step.

Part II: Cementing, Supporting and Veneering Prosthetic Dental Materials

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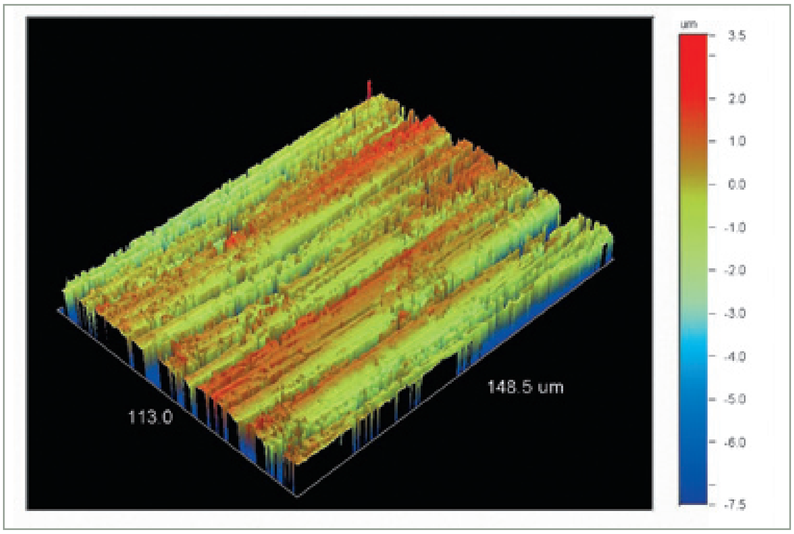

Zirconia surface roughness: 3D image as recorded by optical interferometric profilometry (courtesy of George Eliades).

Introduction

by the Moderator,
Dr Stefano Gracis

Bonding capacity of luting agents to alloys and ceramics

For the successful integration of a restoration in the oral cavity, the act of cementation is a crucial step which influences profoundly the prostheses' longevity. The choice of luting agents has increased over the years, responding to the needs of a market requiring easier handling, less technique sensitivity, shorter setting times, higher retention, insolubility in the oral fluids, antibacterial properties, and improved esthetics. This and a more conservative approach to tooth preparation, which often does not follow the classical rules of retention and resistance form, has prompted the profession to shift to the predominant use of adhesive cements. Furthermore, the clinician's perception is that these cements can potentially improve the seal at the interface between tooth structure and restorative materials.

While the protocols for true adhesive bonding to enamel and dentin with autopolymerizing and dual-cured resin composite cements are well known, there is not as much clarity regarding the surface treatment of different artificial substrates prior to cementation. What is the proper procedure for allowing or enhancing a chemical bond to metals, alumina or zirconia? Are metal primers and silane coupling agents effective, and how should they be handled? Are self-etching cements as reliable as the "traditional" resin cements? Is proper field isolation mandatory and crucial? These are the main topics being addressed in the first Essays (1a and 1b).

Exploring the interface and the reliability of ceramic veneers on metal and ceramic substrates

The successful restoration of teeth and implants requires not only the esthetic integration of the prosthesis, but of course, its long-term clinical performance as well. The longevity of any restoration depends, to a large extent, on the reliability of the materials employed and on the lasting capacity of its luting agent to provide retention and marginal seal.

Up to now, porcelain-fused-to-metal crowns and fixed dental prostheses employing precious alloys has been considered the "gold standard" combination since it reconciles excellent mechanical and physical properties with the ability to deliver, at least in many situations, good esthetics. Its clinical performance and relatively low incidence of mechanical complications has been well documented in the literature.

In recent years, the advent of less expensive alloys and new metal-free ceramic materials and systems seems (or attempts) to challenge this standard. The question that any responsible clinician should pose to him/herself is whether there is evidence that these materials provide a similar degree of reliability. One crucial aspect that has an impact on clinical performance is the quality of the link between veneering ceramic and supporting structure, whether it is made of non precious alloys, titanium, disilicate-based glass ceramics, alumina or zirconia. If this bond fails, adhesive failure of the veneer will occur. Depending on the extent of the chipping, a replacement of the restoration may be necessary. If this complication occurs frequently and within a relatively short period of time after having placed the prostheses in the mouth of the patient, the clinician may suffer an economic damage and, possibly, negative publicity for his/her reputation.

In the recent literature, which has documented zirconia-supported restorations, it is the chipping of the veneering ceramic that has indeed been highlighted as the complication with the largest incidence, varying from 10% to 60% after 5 years of clinical use.

Many hypothesis have been presented to explain such behavior, ranging from the mismatch of thermal expansion between veneering and framework ceramics to insufficient support of the veneering material by the framework design, and from unfavorable surface and heat treatment of the zirconia framework and associated phase transformation to accelerated strength degradation of ceramics. The second Essays (2a and 2b) will address this issue, providing data and recommendations that have an impact on clinical choices and technical protocols.

1. Bonding capacity of luting agents to alloys and ceramics

The Essays

Essay 1a: Clinical interpretation of the scientific evidence

Essayist, Prof Markus B. Blatz

Dental luting agents can be classified into two groups: conventional and adhesive cementation media.[1] Conventional cements, such as zinc phosphate and glass-ionomer cements, simply provide retention for indirect restorations and no or only limited adhesion to tooth structures and dental materials. Still, they reveal excellent long-term clinical success due to some of their other physical, chemical, and biologic properties.[1-3] In certain situations, such as lack of retention, high occlusal dislodging forces, and less-than-ideal marginal fit, clinical success of indirect restorations may be significantly increased through adhesive bonding. In addition, several indirect materials, especially silica-based ceramics, rely on the support and increased fracture strength achieved through strong resin bonds.[4] Adhesive treatment options, such as laminate veneers and resin-bonded fixed partial dentures (RBFPDs), completely rely on strong adhesive bonds.

Adhesive luting agents, typically resin composites, require multiple pretreatment steps to create strong bonding interfaces to the supporting tooth structures and the restorative materials, including metal alloys as well as silica-based and high-strength ceramics. Due to their fundamentally different compositions, these materials require substantially different bonding protocols, pretreatment methods, and materials.

Metal alloys

Adhesive resin bonds to cast-metal and porcelain-fused-to-metal (PFM) restorations (eg, cast post and cores, inlays/onlays, single crowns, and fixed partial dentures (FPDs)), can be increased by fabricating the metal segment with base (ie, nonprecious) alloys. In contrast, the noncorrosive nature of noble and high-noble alloys makes resin bonding more difficult. Various materials and procedures (eg, special alloy primers, tin-plating, and silica coating) increase resin bonds to metal alloys.[5-8] Systems that embed silica particles into the intaglio surfaces of the restorations (eg, Rocatec, 3M ESPE, Berkshire, UK; Silicoater MD, Heraeus Kulzer, Hanau, Germany) have demonstrated excellent bond strengths.[5,7,8] A silane coupling agent is applied to the silicated metal surface for micromechanical interlocking and chemical covalent bonds. Some resin cements contain adhesive monomers that have the ability to chemically bond to metal alloys (eg, Panavia; Kuraray, NY, USA).

Silica-based ceramics

Silica-based ceramics (glass ceramics, feldspathic porcelain, leucite-reinforced feldspathic porcelain, lithium disilicate) are widely used for porcelain laminate veneers, inlays/onlays, and even full-coverage crowns due to their unmatched optical properties. These brittle restorations derive their strength and clinical long-term success from a proper adhesive bond of the definitive restoration to the supporting tooth structure.[4]

A sufficient resin bond to silicate ceramic materials relies on chemical bonding and micromechanical interlocking through surface roughening and silane application. Grinding and air-particle abrasion (eg, aluminum-oxide particles) may increase bond strength, but are not suitable for silica-based ceramics due to the structural damage. Depending on the product and the crystalline content, most studies recommend acid etching of the ceramic surface with 4% to 9.8% hydrofluoric acid (HF) for 2 min.[9] Silane coupling agents provide a chemical covalent bond and micromechanical interlocking.[4,9]

Various characteristics of the ceramic restoration, such as type (veneer, inlay, etc), shade, thickness, and opacity, influence the selection of the resin composite cement. The curing mode (chemical-, photo-, or dual-activated), composition, and viscosity of the resin cement influence clinical handling and physical properties of the bond to the ceramic substrate. Photo-activated resin composite cements are preferred for thin porcelain laminate veneers due to long working times and shade variety. Dual-activated resin cements should be used for silicate ceramic restorations thicker than about 2.5 mm. Strictly chemical-activated composites are used for very thick and/or opaque restorations (eg, metal alloys, alumina, zirconia).[4]

Aluminum-oxide ceramics

Glass-infiltrated and densely sintered aluminum-oxide ceramics (eg, In-Ceram Alumina, Vident, USA; Procera crown alumina, Nobel Biocare, USA) are unsusceptible to bonding protocols successfully applied to silica-based ceramics (ie, HF etching, silane application). Air-particle abrasion and modified resin-based composite cements containing special adhesive monomers (eg, Panavia 21, Kuraray) have demonstrated high bond strengths to glass-infiltrated alumina.[10-12]

Similar protocols can be successfully applied to densely sintered high-purity aluminum-oxide ceramics.[13-17] Long-term bonding studies recommend air-particle abrasion (30–50 µm Al_2O_3) and use of a modified resin cement together with the corresponding ceramic priming agent (eg, Ceramic Primer, Kuraray) containing an adhesive phosphate monomer (MDP).[15,17]

Zirconia ceramics

Numerous studies have investigated resin composite bond strengths to zirconia.[18-27] Whenever resin bonding is needed, airborne-particle abrasion with Al_2O_3 sufficiently pretreats zirconium-oxide ceramics even when applied at a very low pressure. Various studies have shown that the application of a ceramic primer (eg, Ceramic Primer, Kuraray) that contains special adhesive monomers is a crucial step to create long-term durable bonds to the intaglio surfaces of zirconia restorations.[18,22,27] A silica/silane coating (eg, Rocatec and CoJet, 3M ESPE) can also be successfully implemented for zirconia ceramics and allows the use of conventional resin composite cements of choice.[22]

Recently, self-adhesive cements have literally flooded the market with promising prospects. The idea is to obtain decent resin bonds to tooth structures and various dental materials without the additional pretreatment steps. Bonding studies on these cements, however, reveal very mixed results and great variability among the different materials and manufacturers.[28]

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Essay 1b: Experimental evidence

Essayist, Prof George Eliades

Introduction

Modern luting agents may be classified in three major groups based on their composition: (a) water-based cements (zinc phosphate, zinc polycarboxylate, glass-ionomers); (b) methacrylate-based luting agents (MMA/PMMA, dimethacrylate composites) and (c) hybrids (resin-modified glass-ionomers, polyacid-modified resins, glass-phosphonates). The first group sets by an acid-base reaction (cement), the second by free-radical polymerization, whereas the third combines both setting mechanisms.

According to their adhesion capacity, glass-ionomers, glass-phosphonates and resins with acid-functionalized monomers are characterized as adhesive agents.[1] Adhesive resin luting agents are differentiated from their non-functionalized analogues which are essentially combined with a 3- or 2- step adhesive system to mediate adhesion. From all these materials, composite dimethacrylates, including their hybrids, are considered as the strongest, with the lowest solubility offering durable adhesion to dental hard tissues. Nevertheless, the necessity of additional bonding to a variety of substrates (alloys, polymers, ceramics) has established a number of adhesive strategies integrated into different clinical protocols.

Bonding to alloys

Clean alloy surfaces at atmospheric conditions are covered by an oxide layer composed of oxidizable elements. On base-metal alloys, most alloying elements may form surface oxides, mainly basic in character, which may react with acidic groups (phosphate, carboxyl, etc), establishing bonding condition at the interface.[2,3]

Phosphate groups are considered more reactive than carboxyl, although the use of both creates a synergistic effect. On precious alloys, the surface oxides are strongly reduced and thus, the active sites for bonding are diminished.[4] However, thiol groups may bond to precious metals, since it has been identified that Au (under specific conditions) is hydrophilic. These observations have led to the development of a variety of metal primers for bonding alloys with resin luting agents. Some manufacturers designed mixtures of vinyl-phosphate and vinyl-thiol monomers to be used as universal metal primers, while others, to avoid monomer phase separation, synthetized vinyl monomers with both phosphate and thiol groups. Moreover, adhesive resin luting agents have been introduced with phosphate or/and carboxyl-functionalized monomers, achieving high bond strength to base-metal alloy substrates.[5]

To obtain more stable interfaces, high energy treatments have been proposed, like pyrolytic and tribochemical silication treatments, followed by application of silanol coupling agents to form Si-O-Si bonds with the substrate.[6,7] A tribochemical coating can be further used for intraoral repair of exposed alloy surfaces.

From the acid-base cements, glass-ionomers have been shown to induce a weak chemical bonding with base-metal alloys (complexation via carboxyl groups). The hybrids demonstrate improved performance over glass-ionomers, but inferior to resin composites. Recently, the self-adhesive resin composite cements have been introduced, combining the free-radical setting mechanism with the acid-base mechanism of phosphate cements or/and glass-ionomers. Although considered as universal cements, there are great variations in the composition and properties of the commercially available materials, which may affect their clinical performance.[1] Of major importance is the finding that many of these materials demonstrate low C=C conversion, especially after dark setting.[8]

Selection of the proper luting agent depends, as well, on the marginal and internal adaptation of the frames. Full crown alloy frames with tight fit require low viscosity luting agents. In such cases, resin composite luting agents, due to their structure and viscosity, may lead to occlusal interferences. It should be mentioned that the film thickness given according to international specifications is measured under 15 kp load, a value of limited clinical reliability. Furthermore, it has been documented that adhesive luting agents offer the highest strength at a thickness of approximately 100 μm.[9,10] Other luting agents, like glass-ionomers or their resin modified analogues, may be used in cases of tight fitting frameworks.

Bonding to silica-glass containing ceramics

The etching capacity of these structures has established HF etching as the most effective method of creating a microretentive pattern, by taking advantage of the differential acid dissolution of the crystalline from the glass phases.[1] Care should be exerted to avoid overetching and to neutralize any residual acid entrapped in the complex porous structure of etched ceramics. Treatment of these surfaces with silanol coupling agents is considered important to transform the hydrophilic etched ceramic substrate to a hydrophobic one compatible with resin composite luting agents, while concurrently mediating molecular bonding.

From the variety of silanol coupling agents, the ready to use prehydrolyzed materials are more reactive.[1] Since activation of silanols is mediated by low pH, instead of the commonly used acetic acid, modern materials incorporate acidic monomers (mainly phosphate methacrylate derivatives) to provide a synergistic effect. When using silanols on rough surfaces, careful drying should be performed, since these compounds are more reactive in monolayers; otherwise, instead of forming Si-O-Si bonds with the Si-OH bonds of the hydrated ceramic substrate, they produce secondary-bonded siloxane polymers.[11]

From the resin composite luting agents available, light-cured materials with no adhesive monomers are considered to be the best for transparent laminates, providing better color stability and less water sorption, due to absence of polar and highly chromophore chemical groups. Dual- or chemically-cured versions may be used for other applications, where activating light is attenuated by the thickness or the opacity of the restoration.

Bonding to glass-infiltrated and densely sintered ceramics

The very low content or lack of etchable silica phase in materials like glass-infiltrated alumina, alumina and zirconia (Y-TZP), render the previously described treatment inadequate for bonding.[1] Airborne particle abrasion with alumina is commonly used to roughen surfaces for micromechanical bonding. As silanols are not compatible with alumina and zirconia, adhesive composite luting agents with phosphate monomers have been proposed, to provide the highest strength on such substrates, although concerns have been expressed on their long term hydrolytic stability (the main reason being the reduced polarity of alumina and zirconia oxides).

Especially for Y-TZP, the oxygen vacancy left on crystal structure ($Y3+$ replaces $Zr4+$ sites) creates conditions that favor adsorption of polar groups, like phosphates, and may establish a bonding condition, although evidence for such a reaction is still missing. Based on this property, zirconia primers have been recently introduced, containing phosphate- and carboxyl-functionalized methacrylate monomers to be used as coupling agents.[12] The laboratory performance of these primers is still under evaluation. Alternatively, the use of universal phosphate primers dissolved in excess of silanols with thiol components has been recently advised.[13] Although the bonding mechanism is not fully understood, it has been claimed to be quite effective.

Clinically proven methods, like tribochemical silicating, have been proposed for zirconia.[14] However, sandblasting zirconia may destabilize the tetragonal phase and inducing monoclinic phase transformation, then activating the low temperature degradation mechanism.

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Discussion on bonding capacity of luting agents to alloys and ceramics

Edited by Aris Petros Tripodakis and Stefano Gracis

Stefano Gracis

It has been said that silica-based ceramics, and high strength ceramics must be bonded, and that there is no evidence that traditional metal-ceramic crowns and bridges made with precious, non-precious or titanium metal substructures need any bonding, with the exception of adhesive fixed dental prostheses. Let's start the discussion on the use of precious alloys, non-precious alloys and titanium, and clarify if there is any indication to bond these materials.

Tidu Mankoo

Are we talking about luting or actual bonding? Why should we waste time to bond these restorations when we can cement them traditionally?

Markus Blatz

Bonding is recommended for some partial coverage metal-supported restorations, and for full coverage preparations that lack proper retention and resistance form in order to counteract the dislodging forces. Furthermore, bonding can be beneficial for metal cast posts and cores.

George Eliades

It depends on the fit of the post. If the post is a gold post with a good fit, it is better not to bond because the resin film would be too thick. In this situation, a glass-ionomer or zinc phosphate cement would be preferred because their film thickness would be lower. If the preparation does not provide adequate retention, we should not rely on bonding since, in the long run, it will fail. Proper retention and resistance form in the preparation design is still a valid principle that cannot be disregarded, even in the light of the current developments in adhesive systems.

Nicola Pietrobon
So crowns with porcelain margins should be bonded?

George Eliades
If you have a good adaptation, around 20 or 30 microns as usually provided by the precious alloy castings, I don't think there is a need to bond the cervical porcelain. When you use anaerobic Panavia or similar types of cements, you have to be aware that these materials start polymerizing from inside where air is excluded and then, in the end, at the margins. That's why I insist that, for this application, the old traditional systems will work quite well.

Stefano Gracis
If you were to bond precious, non-precious alloys or titanium, how would you treat the inner surface? Is there a difference amongst the three?

Markus Blatz
Yes, there is a difference between the three, based on the ability to create an oxide layer. The best metal to bond to this is titanium because it has a thick oxide layer. It is so thick that it is difficult to control when veneering porcelain. However, for bonding it is ideal since none, or only little surface treatment is needed. With the other metals, a treatment with silica/silane is recommended, for example Rocatec (3M ESPE) or Silicoater MD (Heraeus Kulzer).

Guido Bracchetti
Does it make sense to use metal primers?

Markus Blatz
What I deduce from the literature regarding bonding to metal and metal alloys, is that silica treatment is better than the application of metal primers.

George Eliades
I agree. Silica treatment is much better than the primers, which are not as reliable. Many of them upon application demonstrate phase separation, which is separation of hydrophilic from hydrophobic monomers; therefore, the primer layer is not homogeneous. When resin cements are chosen, the prerequisite is to use a silica treatment (ie, Rocatec) with a silane. Which silane? I would say that the type of the silane is not as critical as drying the field in order to bond to what is called "in-depth absorbed water," that is the strongly bound water monolayer formed on clean surfaces exposed to air.

Just a comment on the new silanes that Markus showed: the Clearfil Ceramic Primer and Monobond Plus are mixtures of silanol and phosphate methacrylate functionalized monomers. These are strong, stronger than the simple silanols and are considered as universal primers for all metals and ceramics. Nevertheless, there is some evidence claiming that the phosphate monomers produce water instability in the siloxane layer formed after silanol condensation. So, we should be careful.

Stefano Gracis
In conclusion, if you want to bond precious or non-precious alloys, your recommendation is to use silica and silane, like Rocatec, plus a silane agent.

Markus Blatz

Yes, but I would always recommend to stay within the product line. For example, if you use the Silicoater MD, use their silane; if you use Rocatec, use their silane. Their silane actually comes in a clear bottle. It is prehydrolized and contains solvents that keep it from polymerizing. If the solution turns milky, it has to be thrown away because the polymerization process has started already.

Stefano Gracis

It has been said that bonding results in a thicker film. Is that so? Is such a statement based upon a clinical feeling, scientific evidence or both?

George Eliades

Film thickness measurement is quite tricky. According to ISO, after mixing the cement, the film thickness is measured under 15 kiloponds load, 10 seconds before expiration of the setting time. This has no clinical relevance at all and not all assessments are made under these conditions. In many cases, specimens are loaded immediately after mixing. Practically, more viscous materials, lacking thixotropy, result in increased film thickness.

For some resinous cements, preheating to 37°C gave the best results, probably due to reduction in viscosity and better conversion, like in the case of Panavia 21 as it has been documented by Matthias Kern. Nevertheless, this material is quite different from Panavia 2F which is dual curing, not taking into account the advantage of the anaerobic setting. The anaerobic setting that was so efficient in Panavia 21 has been strongly reduced in Panavia 2F in order to control the "dark" setting time, assigned to the chemically curing component of the catalyst system.

Stefano Gracis

So, it is true that resin cements have a thicker film?

George Eliades

Yes, in clinical practice.

Stefano Gracis

Many clinicians stress the message that field isolation is necessary for bonding. Resin cements can be used as a cementing medium for the metal substructure of a FPD, but they can also bond. The difference between the two does not depend on the material, but on the procedure and how effective field isolation is.

Markus Blatz

My first statement is that a bad bond is worse than a good cementation. Without good isolation, the real bond strength is not attained and the result may actually be worse than what is obtained with traditional cementation.

George Eliades

Apart from avoiding contact with saliva or blood, the humidity of the mouth has also to be considered when bonding a restoration. Some materials, like the water-based cements, tolerate some degree of humidity, but the adhesive systems that do not usually contain water are very sensitive to humidity. So, it is good to isolate the field as much as possible for bonding. On the contrary, for cementation with glass-ionomer cement, a completely dry field is not necessary.

Thomas Meier
When a crown has received acid etching or a Rocatec treatment in the laboratory and is then contaminated with saliva during trying-in, can it be cleaned or will the surface be compromised?

Markus Blatz
Bonding should start with a clean surface. Surface treatments in the laboratory should be done after trying-in.

George Eliades
A contaminated surface should be cleaned with phosphoric acid and ethanol; remove everything and start the surface treatment from scratch.

Stefano Gracis
What is the surface treatment for bonding alumina?

George Eliades
No efficient sandblasting treatment can be provided for alumina. It is difficult to roughen alumina by air-abrasion because the strongest abrading particle is alumina! It may clean the surface, but is not enough to create a rough morphology, as with other substrates.

Kony Meyenberg
Adhesion requires some kind of roughening. If nothing is done, the surface remains very smooth and, if one of the chemical treatments fails, there will be a problem. In general, physical or chemical roughening is required for all surfaces. My question is if you can give any recommendation for the mechanical roughening of alumina.

Markus Blatz
Not much roughening can be expected by air abrasion on an alumina surface. Still, in order to get good bond strength, some air abrasion is needed because, without any air abrasion, no bond can be achieved. Even with low pressure and small particles, the possibility of adherence is enhanced. Just the presence of alumina splinters on the surface seems to increase the bond strength on alumina.

George Eliades
Actually what happens, from the physical point of view, is that when the alumina surface is attacked by the same material, this is not implanted, but small particle fragments stay on the surface, probably reinforcing a little bit the bond with the resin cement. The topography of the surface is not substantially changed.

Stefano Gracis
So, the consensus for alumina is that air abrasion is recommended, even though it is not very efficient. What about a zirconia surface?

George Eliades
For zirconia, only soft and low-pressure air-abrasion is recommended (chairside, at 1–1.5 bar). Strong sandblasting (in the laboratory, at 3 or more bar) affects the surface by activating tetragonal phase transformation to monoclinic.

Stefano Gracis
So, low-pressure air abrasion combined with a phosphate adhesive is recommended for zirconia.

Danuta Borczyk
If bonding zirconia and alumina is recommended only in order to attain more retention, couldn't some additional mechanical retention be added in the software during milling?

Markus Blatz
Adding this kind of modification during cutting might have a negative effect in the overall physical strength of the material. Another idea is to add a layer of a glass phase by firing it not just on the outside, but on the inner surface as well. This can then be etched and a silica-coupling agent can be used on top of that.

George Eliades
Silanes not only improve bonding, but, first of all, they modify the wetability of the surface in order to avoid porosity at the interface. Silanes do not produce instant bonding, but bond strength increases over time as the setting reaction with the substrate is a condensation type, like the one in condensation silicone impression materials.

Tidu Mankoo
Bonding of a crown implies bonding to dentin. What is the long-term efficacy of this bond?

George Eliades
Considering the long-term efficacy of dentin bonding in operative dentistry, as it was presented by Angelo yesterday, a better performance can be expected under full coverage crowns, where the volume of the resin material is much less and the problem of bulk resin polymerization shrinkage is reduced. On the other hand, water-based cements, like glass-ionomers, create a durable bond as well. Even the phosphate cements, as it has been found recently, may hybridize dentin to an extent, since they are self-etching due to the phosphoric acid.

Bruno Fissore
In the case that a well-bonded crown has to be removed, the procedure is quite complicated. This should make us consider if bonding is absolutely necessary.

Nitzan Fuhrer
Upon removal of an alumina or a zirconia crown, the bond on the tooth surface is found to be stronger than the bond on the ceramic surface. To cut a crown with an inner shell of zirconia is not a big issue. Bonding should be continued because it protects dentin from caries.

Didier Dietschi
Conventional cementation requires a tooth preparation with retention and resistance form. Bonded crowns rely less on this principle.

Stefano Gracis
Whenever you need to compensate for the lack of retention and resistance form in the preparation, there is a stronger indication to bond. While silica-based ceramics must always be bonded, the recommendation for alumina and zirconia is that the individual situation has to be evaluated by the clinician, who will make the final decision choosing between bonding and conventional cementation, taking into consideration the advantages and disadvantages.

Conclusions on bonding capacity of luting agents to alloys and ceramics

by Stefano Gracis and Aris Petros Tripodakis

The following statements can be drawn from the presenters' lectures and the discussion that followed:

1. Traditional alloy substructures of fixed partial dentures can be cemented with any luting agent, but it is suggested to lute them with $Zn_3(PO_4)_2$, glass ionomer (GIC) or resin-modified glass ionomer (RMGIC) that provide the minimum film thickness. The main reason for using composite/adhesive resin luting agents may be an inadequate form of resistance and retention.
2. Silica-based ceramic materials should be optimally bonded with a resin composite luting agent.
3. Silanization is important to improve wetting of the resin-luting agent to the substrate and to establish chemical bonding.
4. High strength ceramics can be cemented with any luting agent. Low-pressure air abrasion (1-1.5 bar) is recommended for bonding. While actual roughening of alumina surfaces cannot be expected, alumina splinters implanted on the surface upon sandblasting seem to increase the bond strength. High-pressure air abrasion (3 or more bar) should be avoided on zirconia surfaces in order to prevent the eventual monoclinic phase transformation.
5. Field isolation is mandatory for bonding: ideally, it should be done under rubber dam, as a minimum, with retraction cord and proper saliva control.
6. Total field isolation is not mandatory if the luting cement is water based ($Zn_3(PO_4)_2$, GIC or RMGIC), but saliva and fluid control are still necessary.

Table 1 A prosthesis made of different substrates can be luted with different types of cements. The table summarizes the possible choices for each substrate.

Prosthesis substrate	Zn-P	GIC	RMGIC	DC-RC	LC-RC	CC-RC
Precious alloys	✓	✓	✓	X	X	✓
Non-precious alloys	✓	✓	✓	X	X	✓
Titanium	✓	✓	✓	X	X	✓
Glass ceramics						
Crowns	X	X	X	✓	X	✓
Inlays/onlays	X	X	?	✓	X	✓
Veneers	X	X	X	?	✓*	X
Alumina	✓	✓	✓	?	X	✓
Zirconia	✓	✓	✓	?	X	✓
Resin composites						
Crowns	X	X	X	✓	X	✓
Inlays/onlays	X	X	?	✓	X	✓
Veneers	X	X	X	?	✓*	X

Zn-P: zinc phosphate; GIC: glass ionomer; RMGIC: resin-modified glass ionomer; RC: resin composite; DC: dual cured; LC: light-cured; CC: chemically cured X: contraindicated;?: possible, but not ideal; ✓: ideal; *: thickness <2 mm (for transparent materials).

Table 2 If a prosthesis is to be luted with a resin composite cement, its surface should be treated as follows:

Substrate	Surface treatment	With what	Pressure	Activator
Precious alloys Non precious alloys Titanium	Air-particle abrasion	30 μm silica-coated alumina particles	~2.8-3 bar	Silane coating
Glass ceramics lithium disilicate based leucite based feldspathic	Acid etching	9% hydrofluoridric acid for 60 sec -5% hydrofluoric acid for 20 sec for lithium disilicate G.C. 60 sec for leucite G.C. 120 sec for feldspathic ceramics	=	Silane coating
Glass-infiltrated alumina	Air-particle abrasion	50–100 μm alumina particles OR	~2.8-3 bar	Phosphate adhesive resin luting agent OR
		30 μm silica-coated alumina particles		Silane coating
Densely sintered alumina	Air-particle abrasion	Alumina particles	~2.8-3 bar	Phosphate adhesive resin luting agent
Densely sintered zirconia	Air-particle abrasion	<50 μm alumina particles OR	~1.5 bar	Phosphate adhesive resin l uting agent OR
		30 μm silica-coated alumina particles		Silane coating
Resin composites	Air-particle abrasion	30 μm silica-coated alumina particles	~2.8-3 bar	Silane coating

Note: Commercially available silica-coating systems that include air-particle abrasion with silica-coated alumina are typically offered in different particle sizes (eg, 30 μm and 50 μm). The 30 micron particle size is recommended for chair-side air abrasion units. Recommended pressure is around 2.8 bar, but some materials may require lower pressure. Therefore, it is important to verify and adjust the pressure of laboratory air-particle abrasion units and chair-side microetchers, which may differ.

2. Exploring the interface and the reliability of ceramic veneers on metal and ceramic substrates

The Essays

Essay 2a: Clinical interpretation of the scientific evidence

Essayist, Prof Markus B. Blatz

Silica-based ceramics, also termed feldspathic porcelains, reveal excellent optical properties due to their high translucency and variety of shade options. Therefore, they are the materials of choice for highly esthetic indirect restorations. Their low flexural strength and inherent brittleness, however, require support from a coping or framework fabricated from either a metal alloy or a high-strength ceramic material. The bond of the veneering ceramic to the core is characterized by the following mechanisms: mechanical interlocking, chemical bonds, and compressive forces.[1] Numerous studies have investigated the metal-ceramic interface and respective bond strengths.[1-12]

The mechanical retention requires a certain roughness of the substrate surface, typically achieved through air-particle abrasion and the ability of the ceramic to adequately wet this roughened surface during the firing process.[5] Chemical bonds are facilitated through the presence of adherent oxides and diffusion of atoms from both the coping material and veneering ceramic into this oxide layer.[1,2,5] Non-precious metal alloys readily form such oxides on the surface, while in noble and high-noble alloys, trace elements migrate to the surface during the firing process, form oxides, and bond to similar oxides in the opaque layer of the ceramics.[6]

The selected alloy should have a slightly higher coefficient of thermal expansion (CTE) than the veneering ceramic. This causes a “draw” of the veneering ceramic towards the coping after firing and puts it under compressive stress, which increases the overall strength of the restoration.[5]

Likewise, this concept has been applied to all-ceramic restorations, especially zirconium oxide ceramics, which have become quite popular.[13-26] Some *in vitro* studies demonstrate that the use of veneering porcelain with a CTE higher than that of the zirconia framework results in delamination of the veneer and formation of massive microcracks.[20] In another study, the shear bond strengths of zirconia/ceramic veneers showed no difference within a CTE mismatch of 0.75 to 1.7 × 10-6°C.[21]

The high bond strength values found in these studies suggest that chemical bonds are established between the two materials. As previously shown for ceramo-metal systems, ceramo-zirconia bond strengths are mainly attributed to the following factors: micro-mechanical and chemical adhesive bonds between core and veneer, CTE values, cooling rate, and geometry of veneered ceramic.[15,21,25,26] Similarly, the CTE of the veneering ceramic should be slightly lower (about 10%) than that of the core material to create compressive stresses in the veneer during cooling.[25,26] Recent studies have used veneering ceramics that were specifically developed for zirconia copings and frameworks.[25,26] Interestingly, many of these studies demonstrate even higher bond strengths of these veneering ceramics to zirconia, as compared to ceramo-metal systems. These findings indicate that the actual bond strength may not the reason for some of the reported "chippings" and fractures of zirconia-based restorations.

Factors often overlooked when examining bond strength as an isolated parameter are modulus of elasticity and flexural strength of the veneering ceramic, in comparison to the coping material. It seems that a "stronger" and more "rigid" veneering ceramic better complements the physical properties of a high-strength ceramic material, causing less chipping and/or fractures.[15,25]

Metal alloys used in dentistry also have a high thermal conductivity, which greatly prolongs the porcelain-cooling rate at the interface and potentially alters the CTE. Applying the exact same firing and cooling parameters may introduce residual thermal stresses in the zirconia and the veneering ceramic, which may translate into cracks and, consequently, failures. Zirconia has very low thermal conductivity and, therefore, requires a significantly adjusted firing and cooling cycles when the veneering ceramic is applied.[21,25]

Lastly, the actual thickness of the veneering ceramic plays an important role in its fracture behavior.[26] Traditionally, high-strength ceramic copings had an even thickness, which may not adequately support the veneering porcelain. The modulus of elasticity and fatigue behavior of zirconia under functional load makes adequate veneer thickness even more important. Therefore, an anatomic coping/framework design that provides ideal thickness of the veneering ceramic has been suggested and has been shown to improve reliability of bilayer all-ceramic restoration. Modern CAD/CAM systems provide excellent tools to appropriately design and verify the most supportive, yet esthetic coping/framework.

Recent clinical reports indicate that successful implementation of the above parameters translates into significantly improved clinical success.[27,28]

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Essay 2b: Experimental evidence

Essayist, Prof George Eliades

Introduction

For decades, porcelain-fused to metal restorations have been the materials of choice for esthetic prosthodontic restorations. Extensive investigations of the porcelain-metal interfaces have disclosed three major mechanisms involved in metal-ceramic bonding: (a) micromechanical retention of porcelain with the rough metal substrate; (b) secondary bonding (wetting) of porcelain paste on the substrate and primary bonding through establishment of surface adherent oxides, that upon porcelain firing react with oxides of the porcelain melt; and (c) compressive forces developed at the metal surface after porcelain cooling due to the tailored mismatch in thermal expansion coefficients (CTE) between porcelain and metal, the former being slightly higher.[1] Recent developments have introduced porcelain application onto high strength ceramic substrates, including glass-containing, glass-infiltrated and densely sintered ceramics. The information on the interfacial reactions involved in such systems is limited.

Porcelain bonding to alloys

The interfaces of noble alloys with porcelain have been the subject of many studies with a variety of analytical techniques to explore the metal-ceramic bonding mechanism. Migration of alloy trace elements (ie, In, Ga, Sn) towards the interface and formation of adhesive oxides with porcelain has been identified as the principal chemical bonding mechanism.[2-4]

On basic alloys, where bulk alloy elements may oxidize as well, a balance between adhesive and spontaneously formed non-adhesive surface oxides is required. For this reason, light elements, highly reactive to oxygen, are incorporated into the alloy to preferentially consume reactive oxidizing species. The thermally controlled balance of all these reactions is very sensitive to temperature fluctuations, leaving a narrow effective temperature range. On Ni-Cr alloys, the surface oxides formed are NiO, $NiCr_2O_4$ and Cr_2O_3 (Cr <30% wt) or mainly Cr_2O_3 (Cr: 30–40%wt). On Co-Cr alloys, the predominant oxide is Cr_2O_3.[5-8] On Ti, to overcome the problem of excessive oxidation, bonding agents are applied containing elements of higher chemical affinity to O than Ti.[9] At the interface, Ti reduces SiO_2 forming oxides (Ti_2O_3, TiO_2, TiO) and complex Ti-Si compounds (ie, Ti_5Si_3).[10,11] For electroformed gold substrates, no chemical bonding exists with porcelain.[12]

Although bonding capacity is usually evaluated by bond strength tests, there is still no consensus on the proper testing methodology, rendering direct data comparison from various studies invalid. Nevertheless, noble alloys seem to offer the highest metal-ceramic strength, followed by base-metal and titanium alloys.[13,14]

Porcelain bonding to glass-containing, glass-infiltrated and densely sintered ceramics

In feldspatic glass-containing (leucite, lithium disilicate, fluorapatite) and lanthanide glass-infiltrating systems, a continuous interface rich in O, Si, Na, K, Ca and La is created during porcelain firing, forming a rather amorphous phase that extends from the veneering material into the inter-granular spacing of glass-ceramics. This layer establishes the primary chemical bonding between core and veneering materials, providing interfacial strength, as confirmed by the frequently mixed type of failures in bond strength tests.[15] Nevertheless, the cohesive strength of these core materials is weak, in comparison with modern high strength ceramics.[16] The latter exhibits a densely sintered polycrystalline structure, free of silica-glass. Consequently, chemical bonding is mostly limited to secondary reactions, with no ionic migration at the interface.

For zirconia, there is lack of evidence on the bonding mechanism with dental porcelain.[17] In industrial applications, though, it has been postulated that melted silica phases may attack Y-TZP intergranular sites and create secondary bonding conditions that facilitate excellent wetting of porcelain on zirconia frames.[18] As these sites are yttria segregation points, reaction with melted silica may destabilize the tetragonal phase dependent on crystal orientation.[19]

A tetragonal to monoclinic zirconia phase transformation after porcelain firing has been confirmed in one study, mainly attributed to the water content of the "wash" porcelain layer applied onto Y-TZP frameworks.[20,21] This phenomenon is actually the onset of zirconia low temperature degradation. Taking into account that some of the currently employed CAD/CAM manufacturing methods have been shown to induce monoclinic transformation in Y-TZP frameworks (not reversible by the porcelain firing temperatures), it may be concluded that at least part of the surface veneered by porcelain is already destabilized.

The relation of this transformation with the clinically documented porcelain failures is unknown. It has been reported that transformation may strengthen the interface (ie, after sandblasting).[22] Nevertheless, the destabilized surface regions may act as a loci of transformation propagation. Due to the resultant volumetric expansion, the stresses may be more easily distributed towards the weaker overlying porcelain than the densely sintered polycrystalline substrate. The tensile components of these stresses may be implicated with bulk porcelain fractures. Besides, evidence of high interfacial residual stresses associated even with the tetragonal phase has been recently reported, which further complicates the detrimental stress-patterns at porcelain-zirconia interfaces.[23]

The higher modulus of the densely sintered alumina and zirconia results in much higher flexural strength of porcelain layered beams, than other core ceramic materials. However, the core thickness may affect veneer fracture. Alumina core, being stiffer, with almost twice the elastic modulus of zirconia, demonstrates less dependence on frame thickness.[16] To improve the performance of Y-TZP, alumina-toughened Y-TZP composites have been designed. Recently, a ceria-doped alumina toughened zirconia nanocomposite has been introduced, with improved mechanical strength and exceptional stability of tetragonal to monoclinic transformation. Porcelain bonding to this substrate is mediated by the same mechanisms as in Y-TZP, with no evidence of chemical interactions so far.[24] The same applies also for ceramics pressed on alumina and zirconia.

In several comparative bond strength studies performed with the same methodology, the results of porcelain bond strength with zirconia were found to be lower than noble alloys.[25,26]

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Discussion on exploring the interface and the reliability of ceramic veneers on metal and ceramic substrates

Editing by Aris Petros Tripodakis and Stefano Gracis

Stefano Gracis
The second issue to be discussed deals with the interface between ceramic veneers and framework substrates. The message that I got from the lecture of Markus Blatz is that he is convinced that CAD-CAM technology is here to stay. On the other hand, the message from George Eliades' lecture is that zirconia as it is now (yttrium reinforced) is not necessarily the end product to be used with CAD-CAM technology, and that there will be further developments.

George Eliades
CAD-CAM is promising not only for ceramics, but also for metals. For example, the casting of cobalt-chrome alloys has always been problematic. CAD-CAM offers tremendous advantages because a framework, which is milled, is much stronger than when cast.

Markus Blatz
That is why, when talking about digital milling, the discussion should not be limited to a specific material, but it should be extended to all the possibilities that CAD-CAM offers today. We can even mill the frameworks for removable partial dentures. The obvious advantage is that the material is much more homogeneous than when cast.

Stefano Gracis
My question is: can all these materials be used to make a substructure that has to be veneered? We have seen more problems with zirconia-supported restorations than we have seen with alumina-supported and, certainly, metal-ceramic restorations. So, one of the issues is whether we should go to full contour restorations.

Tidu Mankoo
No, this is not actually true, at least not any more. What has happened with zirconia is that the profession has been the testing ground in the development of zirconia-based ceramics. Now there is a clear understanding that both the design of the framework and the thickness of the veneering ceramic are critical. The layer of veneering ceramic should be thinner than the one applied to metal-ceramics. The early zirconia frameworks that we designed were like metal-ceramic frameworks: they were too reduced with big chunks of porcelain on top.

Stefano Gracis
I agree with what you just said, but the evidence in the literature is giving a different message.

Tidu Mankoo
We cannot go with just the evidence in the literature. All of the on-going clinical trials that I have seen recently, and the publications of many universities, say the same thing: that the frameworks should be thicker and that the amount of porcelain on top should be decreased.

Stefano Gracis
So here we are: substructure design is a big issue to prevent or reduce the incidence of ceramic chipping.

Tidu Mankoo
The coefficient of thermal expansion (CTE), how the ceramic is heated and cooled, and other factors, also all contribute to the incidence of chipping. When all is under control, it seems that the clinical performance of the zirconia material is the same as metal-ceramics. Many of the studies that have shown a high incidence of chipping used experimental CAD-CAM systems, and materials that have not become commercially available and their framework design is not clear. So, these studies are meaningless from a clinical standpoint. This is the problem with all scientific data that don't have relevance to everyday dentistry.

George Eliades
I agree with Tidu only partially. Initially, the zirconia studies were limited to three years and demonstrated a high success rate. Now that the studies have reached nine years of follow-up, many problems have been pointed out. The chipping incidence, for example, arose from the clinical studies and was not predicted from the material standpoint. I want to see which are the specific developments now and how these developments are going to be included in the new clinical trials. My point is that, as a dentist, I do not want to contribute to the development of a system through the failures that I face in my clinical practice.

Tidu Mankoo
I agree, but that doesn't negate the fact that the material, if we can find out how to use it optimally, has a clinical potential.

George Eliades
Of course. However, as a dentist, I am not going to do that clinically. I want a material to reach my hands, especially these types of materials, which are very different from composites, after proper development.

Markus Blatz
This is a major problem. Don't forget that it took us fifteen to twenty years to figure out how to deal with PFM and nowadays we want zirconia to be fool-proof overnight!

Nicola Pietrobon
The big difference today, as a laboratory technician, is that I have to invest about 100,000 Swiss Francs or 100,000 US dollars (80,000 Euros) to get new equipment. I have to buy now, for the sixth time, a new system while I am still fighting with the others. I am not willing to do this any more. All the problems we are facing now are due to the fact that gold has become so expensive. But you cannot give the public the message: "Face the future! We can go for it!" and then add: "We don't care about failures." We cannot do that!

Aris Petros Tripodakis
Yet, George in his lecture only mentioned half of the problem. A major aspect that he didn't touch upon is zirconia's hydrolytic degradation that happens as aging takes place. I think that he should address this and make us aware about the

influence of water on zirconia frameworks not only 2 to 3 years after insertion, but after 5 or 10 years.

Stefano Gracis
This is a very good issue that we should address. As a matter of fact, I too have a question on this phenomenon, because I have been using zirconia abutments for many more years than I have been delivering zirconia crowns and fixed dental prostheses. In my personal clinical cases, I have never witnessed a zirconia abutment fracture that could be linked or explained by this degradation, even though they are never veneered. So, I would like to ask both of you whether this process has an effect on the material in a clinically significant way and, if so, after how many years should we be expecting to see something.

George Eliades
Zirconia may change phase, from tetragonal to monoclinic, at ambient temperatures or in the presence of water, a phenomenon known as low temperature degradation. This induces surface and subsurface damage, which along with the loading conditions may create problems. Today, veneering ceramic chipping is the predominant failure. Phase transformation may be implicated in such failures, by producing tensile stresses towards the veneering material. To face this problem, monolithic zirconia has been introduced and advertised as problem-free, provided that occlusal surfaces with mirror-like smoothness are produced. Of course, the intraoral stability of such a surface is put in question. We must consider that the primary industrial use of zirconia is for oxygen sensors and fuel catalysts, due to its inherent affinity to oxygen. Then, the question is how reliable can such a material be in the complex intraoral environment?

Andrea Ricci
As clinicians, our approach to the use of zirconia has been wrong. I think that universities and the industry need to test the material and I think that strict protocols should be applied. Nowadays, whoever talks about zirconia has a different approach in using it and treating it. We need long-term studies and sound research centers that can test the material with protocols like Markus's. Until I see those results and I read those publications, I will not use zirconia again.

Stefano Gracis
I would like to ask Markus whether, from his position as a clinical researcher who has been using zirconia for a long time, he recommends using this material to our audience. George was very clear about the fact that he would not recommend zirconia right now.

Markus Blatz
It is work in progress. In our practice, working with our CAD/CAM Center and the select dental laboratories that have gained significant experience with the material, we don't see any greater chipping rates than with PFMs. A lot depends on the laboratory. A critical thing, for example, is the calibration of the milling machines as well as the calibration of the firing ovens. If the oven for sintering is 50 degrees Celsius lower or higher than the optimal temperature, you get a totally different material. So, if you ask me whether I can recommend it to

everyone, I would say no. I would recommend it only to technicians who are familiar with the important handling, design, and firing parameters mentioned before. Some of the early studies that presented a lot of chipping analyzed the behavior of materials, which were experimental. However, more recent studies found fracture rates of zirconia fixed dental prostheses similar to those of porcelain-fused-to-metal (PFM) fixed dental prostheses. They also pointed out that all of these fractures occurred in areas where there was occlusal roughness after occlusal adjustments or wear. This is why polishing is very important. That is true for every ceramic, not just for zirconia; but in the case of zirconia, it may be even more important because of the possible degradation.

Stefano Gracis

The chipping that I observed in my early experiences with zirconia-supported restorations I believe could be ascribed to the fact that dental technicians were not aware that they had to apply different heating and cooling rates compared to metal-ceramics. In this way, a lot of stress was built into the structures. However, there is a range of opinions among dental technicians about what the optimal heating and cooling rates are, and that is another matter of confusion.

Nicola Pietrobon

When you buy a system, the companies do not tell you how to heat or cool zirconia. How can the technician know what he is supposed to be doing?

Stefano Gracis

My last question is whether, to prevent low temperature degradation, it is enough to cover the entire surface of zirconia with the veneering ceramic. Will that help?

George Eliades

No, It may reduce the degradation, but it will not be sufficient. As soon as you fire porcelain on the substrate, the mechanism is initiated and the degradation is there. It is like having a metal that starts oxidation at the interface.

Conclusions on exploring the interface and the reliability of ceramic veneers on metal and ceramic substrates

by Stefano Gracis and Aris Petros Tripodakis

The following statements can be drawn from the presenters' lectures and the discussion that followed:

1. CAD-CAM is the promising technology of the present both for ceramics and metal alloys.
2. Zirconia-based restorations may be recommended as an alternative to metal-ceramic restorations for fixed partial dentures and crowns, taking into account that the relevant material science is still under development. Low temperature degradation is a phenomenon to be considered. Further scientific evidence should be provided relating to the long-term durability of the restorations exceeding

the five years of successful clinical application.

3. Chipping of the veneering ceramic in zirconia fixed dental prostheses is still a clinically relevant problem; however, some factors are better understood today, such as framework design, heating and cooling cycle-protocols during porcelain firing and thus, the incidence is expected to decrease.
4. Porcelain bonding to high-noble alloys has proven to be reliable.
5. Porcelain bonding to non-precious alloys has been improved and is considered reliable as well, although lesser than on high-noble alloys.
6. Porcelain bonding to titanium is the least reliable and inadequate in certain commercially available systems.

Table 3 How to minimize or prevent ceramic chipping on zirconia.

Involved factors	Proposed procedure
Substructure design	It should be shaped to support the veneering ceramic, which should be of limited thickness (<1.5 mm).
Veneering surface roughness	Avoid mechanical damage to the intaglio surface and polish any roughness in the veneering ceramic (ie, occlusal adjustments).
Coefficient of thermal expansion (CTE)	Veneering ceramic has to have CTE optimized for zirconia.
Heating and cooling rates	Lower than for metal-ceramics; need for ovens to be calibrated for zirconia.
Modulus of elasticity of veneer	Veneering ceramics with e-moduli closer to zirconia are preferred.
Low temperature degradation (LTD)	Need for covering all zirconia surface with veneering ceramic.