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The development of resin-bonding for amalgam restorations

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Adhesive techniques are now used for many dental restorative materials, including amalgam. Several generations of dentine bonding agents have been developed, mainly for bonding composite resins. When bonding is used with amalgam restorations, the need for retention and resistance form is reduced, the seal is improved, and some procedures, such as amalgam sealants, which were not previously possible, can be considered.

At a time of rapid activity in the field, this article gives a timely interim overview of the development of resin-bonding of amalgam restorations using adhesive resin bonding agents and chemically-activated luting agents. Consideration of bonding to enamel and dentine is followed by the development of resin dentinal adhesives over several 'generations' of progress to the current multiple-purpose bonding systems of conditioners, primers and adhesives. The specific development and adaptation of bonding resins for metal bonding precedes a brief coverage of some currently popular systems available for use in bonding amalgam restorations. Relevant publications are selected for their practical clinical value, rather than furnishing an exhaustive review of all published literature.

Bonding to enamel using the acid-etch technique

For more than half a century there have been studies focused on caries and acid solubility of enamel, including many in the 1930s and 1940s. However, it seems that the foundation for the popularisation of adhesive restorative and related preventive dentistry was laid in 1955, when Buonocore proposed that acids could be used to alter the surface enamel to 'render it more receptive to adhesives'.[1]

In brief

- Bonding amalgam restorations gives promise for reduced need for mechanical retention features and resistance form which conserves sound tooth tissues.
- Bonding amalgam restorations help to restore tooth integrity and fracture resistance.
- Bonding amalgam restorations assist in the improvement of the marginal seal with potentially less sensitivity.

Subsequent work by Gwinnett and Matsui,[2] and Buonocore *et al.*,[3] suggested that the formation of 'resin tags' was the primary attachment mechanism of resin to phosphoric acid-etched enamel. Acid etching removes about 10 μm of the enamel surface and creates a porous layer ranging from 5 to 50 μm deep. When a low viscosity resin is applied, it flows into the microporosities and channels of this layer and polymerises to form a micromechanical bond with the enamel.

The most widely used etchant is aqueous phosphoric acid (usually 30-50%). It is applied for 15-60 seconds, after which the substrate is thoroughly washed and then dried with an oil free air-stream. Prepared (cut) enamel may be etched for less time than unprepared enamel and still provide a satisfactorily retentive surface for bonding.

Bonding to dentine

Problems in bonding to dentine

Bonding to dentine has been more difficult and less predictable than to enamel. The difficulty in bonding to dentine relates to dentine's complex histologic structure and variable composition. Whereas enamel is 92% inorganic hydroxyapatite by volume, dentine is (on average) only 45% inorganic. Also, in contrast to the regular arrangement of hydroxyapatite crystals in enamel, dentinal hydroxyapatite is randomly arranged in an organic matrix that consists primarily of collagen, which is permeated throughout by tubules. These contain vital processes of the pulp odontoblasts. Hence, vital dentine is a sensitive structure. The high water content provides competition with any adhesive biomaterial for bonding to dentine. Moreover, when dentine is prepared with dental instruments, as in caries removal, the outermost dentine forms an attached surface smear layer (consisting of denatured collagen and debris)[4] which blocks the tubule openings. To achieve a strong bond, it is necessary to either strengthen this smear-layer *in situ* or to remove it entirely. In the latter, it is imperative to ensure an adequately adhesive restorative otherwise the open tubules may allow irritants or bacteria greater access to the pulp.

Development of resin dentinal adhesives

Hagger patented a 'cavity seal' material in 1951. This was a glycerophosphoric acid dimethacrylate and methacrylic acid, which was polymerised using a sulfinic acid initiator.[5] McLean and Kramer investigated this in 1952 showing that the agent penetrated the dentine.[6]

Buonocore *et al.,*[7] also reported more than four decades ago that a resin containing glycerophosphoric acid dimethacrylate could bond to hydrochloric acid-etched dentinal surfaces. The bond strengths of this early method of adhesion were greatly diminished by immersion in water. To overcome this problem, Bowen [8] synthesised N-phenylglycine glycidyl methacrylate (NPG-GMA). However, products based on NPG-GMA had very poor clinical results when they were used to restore cervical erosion lesions without mechanical retention.[9]

A second generation of dentinal bonding agents was developed for clinical use during the early 1980s, but most products are no longer commercially available. Most of these materials were halophosphorous esters of unfilled resins such as bisphenol A-glycidyl methacrylate (bis-GMA) or hydroxyethyl methacrylate (HEMA).[10,11] Shear bond strengths for these materials were considered too low to counteract the polymerisation shrinkage of composite resin.[12] Also, some evidence indicates that bonds between phosphate-based dental adhesives and dentine were hydrolysed by immersion in water.[13]

A major reason that is offered for the poor performance of second generation bonding agents is that they were supposedly bonded to the smear layer rather than to the dentine itself. Hence their bond strength was limited by the cohesive strength of the smear layer or by the adhesion of the smear layer to the underlying dentine.[14,15]

A third generation of adhesives, unlike the second generation, either modify or completely remove the smear layer to allow resin penetration into the underlying dentine. Examples include Scotchbond 2 (3M Dental, St Paul, MN, USA), Gluma (Bayer/Miles, Leverkusen, Germany), Tenure (DenMat, Santa Maria, CA, USA), Prisma Universal Bond 3 (Caulk/Dentsply, Milford, DE, USA), Syntac (Ivoclar Vivadent, Schaan, Liechtenstein), and XR Bond (Kerr, Romulus, MI, USA).[5,11] These adhesives have been clinically effective when used beneath composite restorations and can presumably reinforce tooth structure that has been weakened by disease, trauma or cavity preparation.

Current dentinal adhesives

Several major dental manufacturers have introduced new generations of bonding systems that use etching of dentine with phosphoric acid or other acids. Examples include All-Bond 2 (Bisco Dental, Itasca, IL USA), Amalgambond (Parkell, Farmingdale, CT, USA), Clearfil Liner Bond (Kuraray, Osaka, Japan), ED Primer/ Panavia 21 (Kuraray), Optibond (Kerr) and Scotchbond MultiPurpose (3M Dental), among others.[5,16]

This 'fourth generation' is commonly known as the multipurpose bonding systems because:

1. They can be used in mixed cavities for both enamel and dentine, and
2. Some of their components can also be used for bonding to substrates such as porcelain and alloys (including amalgam). In each case the mechanism of bonding is micromechanical into etched or grit-blasted surfaces.

Components

The components of the 'fourth generation' are a set of chemical agents that proceed in sequence from an initially hydrophilic component (an aqueous, alcohol or acetone solution) through to gradually more hydrophobic components. Specifically, they comprise the following items:

Conditioners

These are generally acid solutions such as phosphoric acid (aq) or dilute nitric acid. Acid etching removes the smear layer, and opens the intertubular and peritubular dentine. Removal of hydroxyapatite crystals leaves a collagen meshwork that can collapse and shrink because of the loss of inorganic support, especially if desiccated. After placement, the conditioner is rinsed off. Many bonding agents, particularly those containing acetone as a solvent, work better on dentine that has been left moist after rinsing.[17]

Primers

A primer is applied after rinsing of the conditioner. Primer molecules such as HEMA (hydroxy-ethyl-methacrylate), biphenyl dimethacrylate (BPDM) and 4-methacryloxyethyl trimellitate anhydride (4-META) contain two functional groups - a hydrophilic group and a hydrophobic group. The hydrophilic group has an affinity for the dentinal surface and the hydrophobic (methacrylate) group has an affinity for resin. The primer wets and penetrates the collagen meshwork, raising it almost back to its original level. The primer also increases the surface energy, and hence the wettability, of the dentinal surface.[5]

Dentine adhesives

These are applied by brush or other means to cover the treated surface to permit resin wetting and penetration. They are unfilled resins that may consist of hydrophobic monomers alone, such as bis-GMA, or may include adhesion promoters to facilitate wetting of the dentine. They attach to both the primed dentine surface and copolymerise with the overlaying composite restoration.

The latest generation of bonding systems combines either the primers and the bonding resins in one bottle, or the conditioner and primer in one bottle. This represents an improvement in convenience, though not necessarily in bond strength. Some examples are: Single Bond (3M), One-Step (Bisco), Prime and Bond (Dentsply) and Liner Bond 2 (Kuraray).

The 'hybrid layer'

Unfilled resin, when applied, penetrates the primed dentine, copolymerising with the primer to form an intermingled layer of collagen and resin, termed the resin-reinforced zone, resin-infiltrated zone, resin-infiltrated layer, or the hybrid layer. Formation of this hybrid layer, as described by Nakabayashi *et al.*[18] in 1982, is thought to be the primary bonding mechanism of most current adhesive systems.

The development of amalgam bonding

Early methods of lining preparation walls for amalgam restorations

The shortcomings of amalgam restorations, including poor appearance, lack of adhesion to tooth surfaces and microleakage are widely recognised. One of the first attempts to improve the retention and seal of amalgam restorations involved painting the cavity walls with a thin coat of zinc phosphate cement and condensing the amalgam immediately onto this wet surface. This technique was described as early as 1897, and positive results were reported in terms of improving the retention and seal of amalgam restorations.[19] However, it never caught on as a standard technique and is only infrequently mentioned in some texts of operative dentistry.[20,21]

A further attempt to improve the interface between amalgam and tooth by bonding was made by Zardiackas in 1976.[22] He developed the so-called 'selective interfacial amalgamation' liner by combining components of polycarboxylate cement with amalgam alloy particles. This liner was tested in tensile adhesion and microleakage tests and found to give tensile bond strengths of around 3.5 MPa, with shear punch bond strengths up to 15 MPa,[23] and to inhibit microleakage as well.[24] For some reason, this process never became popular either, perhaps because the papers were published in journals not read by most clinical dentists.

Further development in amalgam bonding came with the development of metal adhesive resins, originally formulated for bonding fixed partial dentures in the 'Maryland bridge' technique.[25]

As will be appreciated, the bond strengths found *in vitro* have tended to increase with successive products. However, there is still no minimum bond strength that has been definitively shown to satisfy requirements for retention, fracture resistance and other properties. Furthermore, high bond strengths do not necessarily mean low microleakage values for bonding materials.

The development of metal adhesive resin cements and their use for amalgam bonding

The early 'Maryland bridge' technique involved etching the metal surfaces with a chemical or electrochemical process, which was inconvenient, because it required sending the bridge back to the laboratory for etching, after it was contaminated in the try-in procedure. To simplify the procedure, two Japanese manufacturers developed adhesive resin cements, which were formulated with special resin monomers to enhance bonding to metal surfaces after air abrading or tin-plating these surfaces. This procedure can be easily done in the office, thus saving one appointment. The cements were marketed as Sun Medical's 'Superbond' (which was based on the 4-META-TBB adhesive monomer) and Kuraray's 'Panavia' (based on the MDP monomer).

Resin cements as amalgam bonding agents

Soon, researchers in Japan and US began testing these resin cements for use as amalgam bonding agents. Varga *et al.*[26] tested both Superbond and Panavia and found them to bond amalgam to etched enamel surfaces and inhibit microleakage. Bond strengths of up to 17.7 MPa were reported for Superbond. Shimizu *et al.*[27] tested various combinations of Superbond or Panavia in combination with fluoride treatment and glass ionomer cement for amalgam bonding, and found shear bond strengths up to 10 MPa on etched enamel and up to 6.4 MPa on dentine. They also found that Panavia combined with fluoride treatment and glass ionomer reduced microleakage[28] and described the clinical technique.[29]

Staninec[30] tested Panavia for bonding amalgam to both enamel and dentine in a tensile test specifically designed for amalgam bonding. Panavia was found to give bond strengths of 9.7 ± 1.6 and 3.2 ± 0.4 MPa on etched enamel and dentine, respectively, whereas the copal varnish control gave a bond strength of 0.0 MPa. Microleakage was also found to be inhibited, particularly on etched enamel margins.

Since then, many studies have examined the use of not only resin cements, but also a number of dentine bonding agents, for possible use as adhesive liners for amalgam restorations. Some researchers have tested the adhesive liners for improving adhesion and retention, while others have tested only microleakage inhibition, expecting the liners to do no more than improve the seal over the previous standard - copal varnish.

Current adhesives used to bond amalgam

Although numerous commercial products are available for adhesion to enamel and dentine, most of these are intended for use with resin composites. Some of them also have metal bonding capabilities and may be used alone or with additional components for amalgam bonding. A few products have been specifically developed for amalgam bonding. Recently, some dental adhesive resins have shown excellent adhesive properties to both tooth structures and encouraging bonding to amalgam alloys.

Also, in this respect, due to the method of condensing amalgam onto an unset adhesive resin liner, there is an intimate mechanical interlocking created. Some of the main adhesives used in amalgam bonding studies include All-Bond 2 (Bisco), Amalgambond Plus with HPA (high performance additive) powder (Parkell), Optibond 2 (Kerr), Panavia EX and Panavia 21 (Kuraray).

When All-Bond 2 is used, enamel and dentine are both etched with 10% phosphoric acid for 15 seconds. After etching and rinsing, the tooth surface is left visibly moist. This is because drying of the dentine can cause collapse of the unsupported collagen network, inhibiting adequate wetting and penetration by the primer. An unfilled chemically activated resin is placed after the primer.

This material is under study in a prospective, controlled clinical trial along with the All-Bond C&B resin luting cement to bond Nordiska Scania 2000 dental amalgam.[31] The study includes bonded amalgam sealants placed into pits and fissures unprepared, apart from prophylaxis with pumice on a bristle brush and etching with phosphoric acid. A minimal extension bonded amalgam restoration and anatomic dental pits sealed with bonded amalgam are shown at 3-year recalls in figures 1 and 2, respectively.

Bonded amalgam sealants have been shown to be as effective as resin sealants in a clinical study, at least up to 2 years.[32] However, it is not suggested that bonded amalgam sealants are preferable to resin composite sealants. Rather, it is a demonstration of another extension to the utility of the bonded amalgam technique. It is particularly appropriate in sealing adjacent anatomic fissures and pits at the time of bonded amalgam placement.

Amalgambond is based on a dentinal bonding system developed in Japan by Nakabayashi and co-workers[33] more than a decade ago and is very similar to above-mentioned Superbond. Amalgambond uses a solution of 10% citric acid and 3% ferric chloride to remove the smear layer and demineralise the dentine surface. A primer is applied after the dentine is conditioned. Finally, a self-curing methacrylate resin is applied to impregnate the primed dentine. The resin contains an adhesive monomer called 4-META.

Panavia EX is presented as a powder and liquid, whereas Panavia 21 is a paste-paste system, delivered in a dual syringe dispenser that automatically dispenses equal lengths of base and catalyst paste by turning an end knob on the dispenser. Mahler *et al.*[34] conducted bond strength and microleakage tests on several adhesives proposed to produce amalgam bonding, including Panavia EX. They reported that 'of the materials tested, only Panavia showed the potential to both bond amalgam and prevent microleakage'.

Setcos *et al.*[35] are conducting a randomised clinical trial using the Kuraray ED Primer with Panavia 21 to bond Dentsply Dispersalloy. This adhesive is an autopolymerisable composite cement based on the phosphate ester MDP. Its hardening mechanism is anaerobic in nature. This ongoing trial of 113 restorations includes preparations with no deliberate retentive features.

Up to 2 years, three non-bonded restorations were lost due to lack of retention, with no failures among the bonded restorations. With this number of failed restorations, there was no statistically significant difference between the bonded and non-bonded groups ($P = 0.063$, Mann-Whitney U test). However, over longer evaluation periods, bonded restorations may be found to survive better than non-bonded restorations in preparations with no deliberate retention.

Conclusion

While the search for suitable tooth-coloured alternative materials continues, dental amalgam still remains in extensive use internationally. This overview has highlighted the current intense development of materials for bonding dental amalgam restorations that has provided an opportunity for a re-evaluation of preparation design here-to-for based on providing undercuts for mechanical retention. The promise of reliable bonding of dental amalgam restorations enables more conservative restoration of carious destruction ranging from initial lesions, through to complex restorations with cuspal replacement.

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Fig.1 Photograph from a clinical study on bonded amalgam restorations at the third year clinical review. Note the bonded amalgam minimal distal box restoration on the first premolar

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Fig. 2 Additional third year clinical review photograph showing premolar anatomic pits and fissures sealed with resin-bonded amalgam

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