



Dentin Bonding Agents – An Overview

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I. Introduction

Fluid filled channels in some restored teeth provides a continuum between gaps of the walls of prepared teeth structure & around the restorative materials, through dentinal tubules of the pulp. The microleakage dentin sensitivity & pulpal irritation is due to the liquid continuum. The clinical consequences of these problems are decreased by the pulpodentin complex which reacts to the environmental challenges. The structure and function of dentin needs to be reviewed to understand the biologic mechanisms of these responses.

Dentin is a vital part of the tooth, which is formed by the odontoblasts that secretes a collagen matrix centripetally towards pulp chamber, except for a thin layer of pre-dentin in a pulp, this collagenous matrix is subsequently mineralized. A cytoplasmic process extending a variable distance into the dentinal tubules is there in each odontoblast.

During dentinogenesis, dentinal tubules are forced close together. The volume of dentin at the pulp chamber is lesser than the volume of dentin at the dentinoenamel junction. There is a profound influence on both, the structure of dentin & its function due to the convergence of the tubules towards the pulp chamber.

Each dentinal tubule located at the DEJ, is an inverted cone with a smaller diameter (0.5 to 0.9 μ m) which increases to 2 to 3 μ m at the pulp. The increasing tubule diameter in deeper dentin with the convergence of the tubules on the pulp chamber, produces an exponential increase in dentin permeability as dentin is prepared deeper. Dentinal tubules are very long with channels that is 3 to 3.5mm thick (3000 to 3500 μ m)¹.

II. History Of Dentin Bonding Agents

In 1955, Buonocore was the first who reported that the surface of the enamel can be altered by acid, which renders it more receptive to adhesion. He discovered that the human enamel could be bonded to that of acrylic resin after 85% phosphoric acid conditioning. Buonocore predicted some uses for this new technique, including pit & fissure sealants and class III and class V restorations.

Development of dentin adhesives was very slow until 1950s. Bowen synthesized a 'surface active comonomer' that can mediate water resistant chemical bonds of resins to dentinal calcium. But these commercial products based on this comonomer gave very poor clinical performance.²

There has been variations over the past 45 years in dental bonding systems is application chemistry technique, mechanism & effectiveness. This accompanied development of improved composite resins & ceramic esthetic dental materials & in increasing demand by patients for esthetic dentistry. All indirect restorations require or are candidates for bonding. The evolution of bonding agents has increased as the demand for bonded esthetic restorations has continued to increase.³

Dentin Factors

This includes microstructural features of the dentin involved with local adhesions:

- Dentin tubules density size & length
- Smear layer
- Dentin sclerosis

The smear layer of the dentin contains partially denatured collagen that came mostly from the underlying dentin and hydroxyapatite crystals. Generally it is 1-5 microns thick. Although, the smear layer is partially porous hydraulic conductance studies show that it decreases the fluid flow from the underlying dentinal tubules.

Therefore, the smear layer of the dentin acts as a "biological band-aid" reducing tooth postoperative dentistry. This is the consistent process with Brannstroms hydrodynamic theory. This layer requires a drier surface for adhesion and most early dentin adhesives were bonded to this surface.

Adhesion is affected by the wetness of the dentin which is related to size & density of dentinal tubules, which ranges from 20,000 to 50,000 tubules per square millimeter. The density is 30,000 tubules per square millimeter at a level 2mm from the pulp with a diameter of 1.1 microns. Comparatively density of the tubules is greatest near the pulp, because dentin & its tubules are radically concentric to the pulp whereas the tubules near the pulp are the least narrowed due to peritubular mineralization. Tubules shows much larger portion of the



dentin volume (4vol% at DEJ & 28 vol% along the pulpal wall) which immediately wet the cut dentin surfaces. Deep dentin adhesive bond strengths are lower due to the interferences of moisture from tubules. Hydrophilic monomers are included in newer dentin bonding agents that penetrate surface moisture & finds a way around this problem. Hypersensitivity persists if the tubules orifice remains open as there is an increase in dentin permeability & bacterial infiltration. Sensitivity reduces when tubules are occluded with crystalline deposits. This phenomenon can be induced artificially with desensitizing agents that facilitate precipitation of calcium oxalate or other crystals in the dentinal tubules or it can occur naturally through deposition of hydroxyapatite crystals.

It is very important for the clinicians to recognize differences in dentin composition before planning restorations depending on the dentin bonding.

Duke proposed a visual classification for dentin sclerosis:-

(Category 1) - If dentin nominally appears light yellow or whitish & is opaque, then there is no sclerosis present category.

(Category 2) - More than category 1 but < 50% of way between 1 & 4.

(Category 3) - Less than category 4 > 50% of way between categories 1 & 4. .

(Category 4) - If dentin is dark yellow or discolored & appears glassy or translucent then there is a significant sclerosis. It is found more in older individuals.⁴

III. The Acid Etch Techniques

According to Buonocore enamel is bonded with acrylic resin and conditioned with 85% phosphoric acid for 30 seconds. Gwinett & Matsui and Buonocore & others did a subsequent work suggested that the “resin tags” was formed by the primary attachment mechanism of resin to phosphoric acid-etched enamel. The enamel surface is removed about 10µm by acid etching, which creates a porous layer 5-50µm deep. Low viscosity resin flows into the channels & microporosities of this layer, which polymerizes to form a micromechanical bond with the enamel. The surface area and the wettability of the enamel substance can be increased by etching.

Three patterns of etching in enamel-

1. **Type 1** etching pattern involves removal of enamel prism cores while the prism peripheries remains intact, this is the most common type.
2. **Type 2** etching pattern is the reverse process in which peripheries are removed and cores are left intact.
3. **Type 3** etching pattern includes areas which resembles each of the other patterns as well as areas where etching pattern appears unrelated to prism morphology.

Silverstone reported that the enamel surface that have the most retentive appearance which is provided by the 30% to 40% phosphoric acid concentration, until the acid concentration reaches 40%, which increases the calcium dissolution and etching depth. Less amount of calcium can be dissolved by stronger solution which results in smaller etching depth. Let us review dental adhesives according to their generations with its characteristics.⁵

First generation dentin bonding agents

The first generation bonding agents were used in 1960's. These ignored the smear layer and did not recommend etching the dentin. NPG-GMA (N-phenylglycine glycidyl methacrylate), cyanocrylates and polyurethanes were included. The bond strength of first generation dentin bonding agents was 2 to 3 MPa. A 6 month study repeated a failure rate of 50% in the clinical trials. Additional problems included lack of stability of individual components during storage and loss in bond strength over time.^{3,5}

Second generation bonding systems

Second generation bonding agents performed better results than first generation bonding agents and were used in late 1970's & early 1980's. These systems leave the smear layer largely. The bond strength ranges from 4.5 to 6 MPa, these reported a failure rate of 30% in the clinical trials.

These are of 3 types-

1. Phosphate ester dentin bonding agents
 - The phosphate group bonds with calcium in the tooth structure while the methacrylate end of the molecule bonds with the composite resin.
 - This group uses analogs of BIS-GMA with attached phosphate esters.
 - Bond strength 10-30% which is strong as similar to the etched enamel to resin bonds.
2. Polyurethane dentin bonding agents
 - This group was based on the isocyanate groups of polyurethane polymer which bonds to groups of dentin such as amino, carboxyl & hydroxy groups.



- The presence of fluid in the dentinal tubules or smear layer is not affected by polyurethanes setting reaction. The smear layer was left intact by most of the systems, but some involved hydrogen peroxide for cleansing.
3. Etched tubules dentin bonding agents
- This group used 25% citric acid for etching the tubules & included ethylmethacrylate to mechanically interlock with the etched tubules to achieve retention to dentin.⁶

Third generation dentin bonding agents

- This group removes the smear layer before bonding & gives bond strengths ranging from 16-26 MPa.
 - In 2 years clinical retention rates of 100% have been reported.
 - 3 components are used i.e. conditioner, primer and adhesive
1. **Conditioner** – It is a low concentration of a stronger inorganic acid (eg-phosphoric or nitric acid), or a chelating agents (eg-EDTA) and a weak organic acid.
 - It removes the smear layer demineralizes dentin, exposing the collagen fibrils & increases dentin permeability.
 2. **Primer**- It is a bifunctional monomers (i.e. it has one hydrophilic end and one hydrophobic end) in a volatile solvent such as alcohol or acetone. It includes HEMA, NMSA, NPG, PMDM & 4-META.
 - It promotes infiltration of demineralized peritubular and intertubular dentin by its own monomers, adhesive resin and links hydrophobic adhesive resin to hydrophilic dentin. It increases wettability of conditioned dentin surface to increase contact of dentin to resin.
 3. **Adhesive**- It promotes bond strength. It is an unfilled/partially filled resin which may contain some components of primer.
 - It forms resin tags to seal dentinal tubules and provides resin composites to bond with methacrylate groups.⁶

Fourth Generation bonding agents

This group was introduced in 1990's including a primer acid etching agent and an adhesive which are individually applied in a sequence.

That etchant removes hydroxyapatite amongst the collagenous fibers both within the dentinal tubules as well as on the surface of the cut dentinal tubules. The surface was treated with a primer after washing & drying. The dentin primer was so designed that it removes the intercollagenous water filling in the areas created by the process of etching. The final step is to apply the adhesive agent.

The results were highly effective with shear bond strengths of 25 MPa to both enamel as well as dentin. Fusayama & Nakabayashi also described the penetration of resins into dentin as giving dentinal seals with high bond strengths. Kanca also introduced the "wet bonding" concept with these systems.^{3,7}

Fifth Generation Bonding agents

The number of manufacturers began to market a new generation of adhesives in mid 1990's, in which they combined the steps of placing the primer and adhesive while maintaining the high strength. Fresh chemistry for each procedure were provided by the unit-dose packaging during this era. But still surface wetness etching and resin placement is a clinical challenge for clinicians.³

Sixth Generation Bonding Agents

This generation bonding agents were introduced in late 1990's & early 2000's which was also known as 'self etching primers' which made a dramatic leap forward. Self etching step was eliminated, instead acidic primer was included which was placed after the tooth preparation. Some of the variations involved either leaving the primer on the tooth and then placing adhesives over it or mixing the acidic primer and adhesive before placement on the enamel and dentin. The incidence of post treatment sensitivity was reduced in this system compared from the previous systems, but the bond strength is lower than fourth and fifth generation system to enamel and dentin.³

Seventh Generation Bonding agents

This generation was introduced in the early 2000's, eliminating separate etching steps & containing acidic primers and adhesive monomers in a single bottle. Earlier this generation was available as light cured formulations, but now several dual cured products are offered.



The smear layer was used as a bonding substrate. The smear layer and the top layer of underlying dentin surface is demineralized by acidic primer. The exposed collagen along with hydrophilic monomers is infiltrated by acidic primer which then is copolymerize.

The demineralized smear layer is incorporated into the hybrid layer as the etched surface is not rinsed. The hybrid layer thickness is 0.5µm to 5µm. Collagen fibers is infiltrated by the acidic primers and adhesive monomers, as the primer decalcifies the inorganic component in dentin to the same depth, which should minimize potential leakage, postoperative sensitivity or voids. Light cured bonding agents are recommended for bonding of direct light cured resin composites. Light cured products are not recommended for use with self cured core materials and resin cements, due to the acidic monomers. The catalysts associated with self cured resin composites are deactivated by the acidity of these bonding agents & inhibits polymerization.⁸

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