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A REVIEW ON A CONNECTING LINK -DENTIN BONDING AGENTS

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ABSTRACT

Restorative dentistry plays a key function in the field of dentistry in restoring the tooth tissue to its structure, function and esthetics. It helps in maintaining the physiologic reliability in harmony with the surrounding hard and soft tissues. Numerous restorative material did not adhere to enamel and dentin by physical and clinical interactions. Due to this there is increase in the chances of microleakage at restoration tooth interface. Dentin bonding agents have evolved through different generations. There have been changes in chemistry, mechanism, application technique and clinical effectiveness of bonding agents. This review describes about different dentin bonding agents, its evolution, mechanism of action and its commercially availability.

KEYWORDS: Restorative, Esthetics, Dentin Bonding Agents, Etching, Microleakage.

INTRODUCTION

The creation of a steady extended term bond to the tooth material is an ideal requirement for the achievement of all restorations. An adhesion permits the placement of a more conservative restoration, reduces microleakage and dentin sensitivity. A solid knowledge of biological, chemical and physical aspects of all these adhesives is very necessary for their appropriate use in field of dentistry.[1,2]

Dentin is a critical part of the tooth, which is produced by the odontoblasts that secretes a collagen matrix centripetally towards pulp chamber, apart from for a thin layer of pre-dentin in a pulp, this collagenous matrix is then mineralized. A cytoplasmic process extending a variable distance into the dentinal tubules is there in each odontoblast. During dentinogenesis, dentinal tubules are enforced close together. The volume of dentin at the pulp chamber is slighter than the volume of dentin at the dentinoenamel junction. There is a thoughtful 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 0.9µm) which increases to 2 to 3 µm at the pulp. The rising tubule diameter in deeper dentin with the junction of the tubules on the pulp chamber, produces an exponential raise in dentin permeability as dentin is prepared deeper. Dentinal tubules are very lengthy with channels that is 3 to 3.5mm thick.[3]

Adhesive resins are designed to offer strong coupling between resin composites and enamel and dentin. The most primitive dental adhesives were relatively hydrophobic and were placed straightforwardly on enamel and dentin smear layers even though the occurrence of these layers were unidentified at that time.[4]

History of dentin bonding agents

After the success of adhesion to enamel through acid etching by Buonocore in 1952, adhesion to dentin was the main concern as most of the materials used than such as silicate cements, unfilled resins lacked this property.[5] First reports of in vitro studies were those by Kramer and Mclean in 1952 and Buonocore in 1955. Kramer and Mclean speculated that the material used might contain a methacrylic acid.[6] The adhesive described by Buonocore was essentially a dimethacrylate with appended phosphate groups. The groups bonded to calcium of tooth via ionic bonding (chemical bond). Bond strength reported was 5.7 Mpa. Bonds were hydrolytically unstable.

In 1965 Bowen[7] described a system containing surface active N-phenyl glycine glycidyl methacrylate (NPG-GMA) to enhance wetting of the dentin surface and thereby improve adhesion – This was the first generation system. Later second generation system changed the calcium phosphate – resin concept by modifying the resin such as BIS-GMA. These were also not reliable clinically. Later in 1980's a series of solutions were used to increase the wettability of the dentin surface before application of the resin. These systems used more hydrophilic resins. Other systems like GLUMA contain HEMA and glutaraldehyde.

Glutaraldehyde reacted with amino acids of collagen to form charged compounds which than reacted with hydroxyl (OH-) ion of HEMA by mechanical interlocking. This was the third generation of dentin bonding agents.

Eick 1970 described the nature of the smear layer.[8] Fusayama., *et al*. 1979 were the first to report the successful use of phosphoric acid to remove smear layer, etch the dentin and restore with adhesive composite.[9] In 1982, Nakabayashi and colleague used 3% ferric chloride in 10% citric acid as a conditioning agent to remove the smear layer and to demineralize the underlying intact. Kanca 1991 introduced the All etch technique.[10]

Definition of dentin bonding agents

The dentine bonding agents are di or multi-functional organic molecules that contain reactive groups which interact with dentin and the monomer of the restorative resin.[11,12]

Dentin Adhesive System: Components of dentin adhesive systems

The three main components are

a) Conditioner.

b) Primer.

c) Bonding agents / adhesives.

A) Conditioners: Definition: Conditioning of dentin is defined as any alteration of the dentin done after the creation of dentin cutting debris usually termed the smear layer.

Objective: To create a surface capable of micromechanical and possibly chemical bonding to a dentin bonding agent.

Smear layer removal: The initial dentinal surface available for adhesion is covered with a smear layer. This layer is created whenever a dentin is cut or ground and it consists of debris that is smeared across the dentinal surface. It is approximately 1.0mm thick although the thickness may vary depending upon the instrument used in cutting process. Along with the smear layers the cutting process results in plug of debris that can extend several micrometers into the tubules.

The smear layer and smear plugs thus acts as barrier to the fluid movement to the surface via the tubules and may also limit the access of microorganisms and toxins to the pulp. Removal of the smear plugs increase the permeability of dentin 5-20 times (Pashley 1989) and the following fluid movement would then be detrimental for adhesion.

Dentin permeability changes due to conditioners: Conditioner removes the smear layer thus resulting in an increased permeability of dentin. The depth of decalcification and removal of smear layer is affected by various factors including pH concentration, viscosity and application time of etchant.

2. Demineralization effects of conditioners on dentin surface

The conditioning agent present in certain dentin bonding agents not only remove the smear layer, but also cause demineralization of underlying dentin. Some demineralization may be favourable in order to open up the collagen network and facilitate monomer infiltration but the question then arise as to how much of demineralization is essential for optimum adhesion. It has been stated that demineralization depths of 10-15mm are first adequate and below this it is doubtful whether the monomer would effectively penetrate. The demineralization of dentin to a depth greater than monomer can infiltrate and reinforce the collagen network, can lead to decreased adhesion, causes collapse of meshwork. The tooth surface is dried (not desiccate).

B) Primer: Definition: Primers are defined as chemicals capable of improving the wettability of adherents or capable of being incorporated into the surface of the substrate to form chemical bonds across the interface (Causton, 1982). The distinction between conditioners and primers is often arbitrary. Acids have been considered dental conditioners and HEMA solutions have been called “Primers”. Whenever an acidic agent is applied to the dentin surface, it either removes, dissolves or modifies the smear layer and partially demineralize the dentin surface. This creates the space within the collagen network by dissolving or removing the calcified apatite crystals and is roughly analogue to the microporosity created by etching the enamel. Once the acid is rinsed off after an appropriate treatment time unlike the enamel, this treatment of dentin produces a low surface energy. This in turn makes the dentin surfaces difficult to wet with normal bonding resins. In order to correct this a primer is necessary.

Role of primer

Increases the surface wettability and spreadability of the monomer. Stabilize the collagen fibers. Restores the surface energy. Enhances the monomer penetration.[13]

Examples

1. HEMA – Hydroxy ethyl methacrylate.
2. 4META – 4 Methacryloxyethyl trimellitic anhydride.
3. BPDM – Biphenyl dimethacrylate.

Dentin bonding agents can be classified into six groups of compounds[14]

a) Polyurethane.
b) Polyacrylic acids.
c) Organic phosphates.
d) Mellitic anhydride and methyl methacrylate (4-META).
e) Hydroxyethyl methacrylate plus glutaraldehyde (HEMA + GA).
f) Ferric oxalate and NPG-GMA (N-phenyl glycerine and glycidal methacrylate) and PMDM (pyromellitic dianhydride and 2-hydroxyethyl methacrylate).

Polyurethanes

The urethane bonding type is formed by the reaction polyol and dis-cyanate. The object is for the diisocyanate to react with the polyol and the –OH or –NH2 groups in the dentin mineral or organic components. The composite can then bond to the polyurethane.

Polyacrylic acids

These are comparable to the polymers used in Glass ionomer cements and are copolymers of acrylic and itaconic acids. The claim is that these organic acids attach irreversible to hydroxyapatite in dentin by displacing the phosphate ions. The composite then attaches to the polyacrylic acids.

Organic phosphonates

The phosphonate bonding type may or may not be halogenated. It is claimed that phosphate end reacts with calcium in hydroxyapatite and the C = C double bond at the other end reacts with the composite.

Mellitic anhydride plus methyl methacrylate

The mellitic anhydride is dissolved in methyl methacrylate and is referred to as 4-META. The objective is for the anhydride to hydrolyse to a diacid with – OH groups on the surface of dentin and function like an acrylic acid the carbon- carbon double bond will react with the composite.

Hydroxyethyl methacrylate and glutaraldehyde

The glutaraldehyde reacts with an amino group in the organic portion of dentin and also reacts with HEMA, which in turn will react with the composite through carbon double bond.

Ferric oxalate – NPG-GMA / PMDM systems

The ferric oxalate removes the smear layer from dentin and serves as a mordent, while the NPG-GMA and PMDM bond to the dentin and contain carbon-carbon double bonds to react with the composite.[14]

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-

Type 1 etching pattern involves removal of enamel prism cores while the prism peripheries remains intact, this is the most common type.

Type 2 etching pattern is the reverse process in which peripheries are removed and cores are left intact.

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.[15]

Classification

Dentin bonding agents have evolved through different generations during the past few decades. Dentin bonding agents have been categorized into generations of products based on chemistry and the manner in which they treat the smear layer.

The First Generation products were early, largely unsuccessful attempts at producing a bond between dentin and resins. They essentially ignored the smear layer. The Second Generation depended upon the smear layer for bonding while the Third Generation agents characteristically remove or heavily alter the smear layer prior to bonding.[16]

First generation dentin bonding agents

The first generation dentin bonding agents were developed in the early 1960's . Buonocore., *et al*. in 1956 reported that Glycerophosphoric Acid Dimethacrylate (GPDM) could bond to hydrochloric acid-etched dentin surfaces However, the bond strengths to dentin attained with this primitive adhesive technique were only 1 to 3 MPa.

The development of N-phenylglycine glycidyl methacrylate (NPG-GMA) was the basis of the first commercially available dentin bonding agent, Cervident (SS white).They bond by chelation with calcium .The factors like Difficulty in bulk polymerization of the Cyanoacrylates, instability of NPG-GMA in solution in combination with very low bond strength prevent the successful use of these bonding agents.[16,17]

Second generation dentin bonding system

In general, these were improved compared to the first generation bonding agents. The agents used were: Halo phosphorous esters of Bisphenyl A glycidal methacrylates (BIS-GMA).

The second generation dentin bonding agents were developed in the late 1970's and early 1980's These systems leave the smear layer largely, if not wholly, intact when used. Second generation bonding agents produced variable results; they generally performed better than first-generation bonding agents. They routinely produced bond strengths that ranged from approximately 5 to 6 MPa Ethylmethacrylate, Phosphate ester, Polyurethane were incorporated in them.

Brands

Bondlite, Creation Bond, Prisma Universal Bond, and Scotchbond.

Disadvantages in this type were low bond strength, hydrolysis to oral environment and poor wetting leading to failure in restoration.[17,18]

Third generation bonding systems

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, or a chelating agents 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 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.[19]

The third generation dentin bonding agent were designed not to remove the entire smear layer but rather to modify it prior to dentin bonding agent application. With this system, dentin is etched with an aqueous solution of 10% citric acid and 3% ferric chloride, followed by the application of an aqueous solution of 35% HEMA and a self-curing adhesive resin containing 4-META, MMA, and trin-butyl borane (TBB), the last as a polymerization initiator.[10]

Thus the third generation bonding agent came out with a system consisting of Conditioner, Primer and Bonding agent. This paved the way for the further development in bonding agents.

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.[20,21]

Essential to the enhanced adhesive capacity and responsible for the improved clinical effectiveness of fourth-generation adhesive systems is the pretreatment of dentin with conditioners and/ or primers that make the heterogeneous and hydrophilic dentinal substrate more receptive to bonding. The fourth-generation adhesive generally come with 30% to 40% phosphoric acid gels and is referred to as three-step etch-and-rinse adhesive. The total etch technique permits the etching of enamel and dentin simultaneously using phosphoric acid for 15-30 seconds. The surface must be left moist however, in order to avoid collagen collapse.

The fourth generation can be used in cavities for both enamel and dentin. Some of their components can also be used for bonding to substrates such as porcelain and alloys.

Representative adhesives in this group include All-bond 2, Optibond FL, Permaqui (Ultra dent), and Scotchbond Multipurpose etc.Composition of some of the commercially available fourth generation bonding agents are All Bond 2, Scotch bond Multipurpose.[17]

Fifth generation denting bonding systems

The distinct characteristic of the so-called fifth generation is the combination of the primer and bonding resin application steps to achieve bonding with a one component resin formula.

These systems rely on the hybridization of dentine for achieving adhesion.

Because of the complexity and number of steps of compounds involved with the fourth-generation systems, researchers and manufacturers have worked to develop simpler adhesive systems. In this generation bonding agent include etching enamel and dentin simultaneously with 35-37% phosphoric acid for 15-20 seconds followed by application of one bottle containing primer and bonding agent which has a general composition of HEMA, Bis-GMA, dimethacrylate, patented polyalkenoic acid copolymer, Water and ethanol. Though they require fewer steps in achieve dentin bonding, these agents are inferior to fourth generation bonding agents in terms of their bond strength.[22]

Representative commercial products of this generation include excite, One-step, Opti-Bond Solo, Prime and Bond, and Single Bond or Scotchbond.

Sixth generation dentin bonding system

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.[20]

Example – Clearfil bond 2system (Kurrary Co.). In this etchant and primer are combined. Also known as self-etching primer. It contains phosphate derivatives of hydrophilic monomer such as phenyl-P (20-25%). It also contains 50% HEMA or other hydrophilic monomer, so they both etch and primer the dentin. Self-etching primer must have sufficient acidity to overcome the buffering potential of the dentine, but they must also, contain sufficient monomer to compete with water when they diffuse through the smear layer. As the smear layer might not be totally removed by these systems, the partially demineralized smear layer becomes incorporated into a hybrid layer. Thus, self-etching primer produces a thinner hybrid layer than systems using etchants such as phosphoric acid. This does not have any effect on the bond strength.

Representative sixth-generation two-step self-etch adhesives include AdheSE, clearfil SE Bond and clearfil Protech Bond, Opti- Bond Solo Plus.

Seventh-generation adhesives

The newest generation of adhesives consists of single-component, one-step self-etch adhesives, Seventh-generation adhesives combine conditioning, priming and application of adhesive resin, but unlike sixth-generation adhesives they do not require mixing. As a result, adhesives belonging to this generation are intricate mixes of hydrophilic and hydrophobic workings. So far, a number of shortcomings of the seventh-generation adhesives have been documented but to the complex nature of the mixed solutions, the seventh-generation adhesives have attained consistently lower bond strengths that the fourth- and fifth generation adhesives. Representatives of seventh – generation adhesives include Clearfil S Bond (Kuraray), G-Bond (GC), i-Bond, and Xeno IV (Dentsply).[17]

CONCLUSION

The dependability of dentine bonding has enhanced during 1990s and as a effect the number of ulterly invasive techniques accessible to the restorative dentist has improved. It may be projected that the effectiveness of adhesive technique to be dentin will develop further and that in due course all restorations including crowns will be placed using an adhesive procedure and that reattachment technique will become the accepted mode of treatment for fractured cusps and teeth.

The excellent uses for current-generation dentin bonding agents are prior to the luting of cast ceramic, composite restorations with resin cements when dentin is exposed; advantages may include increased bond strength, reduced microleakage, reduced post-treatment sensitivity.

Dentine adhesive systems have created a new era in the field of dentistry. Owing to its property of adherence to the tooth structure by both micromechanical and chemical means, if finds a wide range of application in various fields. It has lead to the most desired forms of treatment needs, which is the conservation and esthetics of tooth.

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