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All about Dentin bonding agents: the connecting link

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Abstract

Restorative dentistry plays an important role in the field of dentistry in restoring the tooth tissue to its form, function esthetics and in maintaining the physiologic integrity in harmony with the surrounding hard and soft tissues. Many of the restorative material used did not adhere to enamel to dentin by physical and / or clinical interactions thus increasing the chances of microleakage at restoration tooth interface. The following article presents a review on dentin bonding agents: and its future considerations.

Keywords: dentin bonding agents, etching, microleakage, HEMA, META

Introduction

The production of a stable long term bond to the tooth substance is an ideal requirement for the success of all restorations. An adhesion permits the placement of a more conservative restoration, reduces microleakage and dentin sensitivity. A solid understanding of biological, chemical and physical aspects of these adhesives is very essential for their proper use in field of dentistry^[1, 2].

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^[3]. 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^[4]. 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 5.7Mpa. Bonds were hydrolytically unstable.

In 1965 Bowen^[5] 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.

Literature Review: An extensive research was done in medline and index medicus data bases on Dentin bonding agents using following mesh words like dentin bonding agents, etching, microleakage, HEMA, META from the year 1973 till 2009 and 67 articles were found out of which 12 articles were reviewed as per relevance for the present research paper.

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^[6, 7].

Requirements of dentin bonding agents: When developing a clinically acceptable dentin bonding agent following goals must be met. Bond strength – The adhesive should be capable of achieving acceptable bond strength to withstand the stresses caused by polymerization

contraction of composites. Optimum bond strength → 17Mpa – 20Mpa. Biocompatibility of the material. The adhesion used should be biocompatible with structures in contact with it. Long-term durability of the bond it is a highly desired factor. Prevents microleakage by reduced gap formation between tooth structure and restorative material. Prevents recurrent caries and marginal staining. Be easy to use and minimally technique sensitive. Have a reasonable shelf-life.

Adhesion: It is a process of solid and / or liquid interaction of one material (adhesive/adherent) with another (adhered) at a single interface. Most instances of dental adhesion are also called “Dental Bonding”. Adhesive is defined by the “American society for testing and materials” as a substance capable of holding materials together by surface attachment. Adhesion is a fundamental objective universal to most restorative procedures [8].

Requirements for adhesion: These must be good wetting in order to produce good bonding & surfaces to be joined must be cleaned.

Chemistry of adhesive agents: The dentin adhesives are characterized by containing monomers that have hydrophilic or hydrophobic groups. The polymerized adhesive system should provide a stable link with structure and bulk of the restoration.

Adhesion of Restorative Resin to Dentin: To obtain bonds of desired strength specially formulated dentin bonding agents must be applied to the conditioned dentin before resin placement.

Dentin bonding agents may act: By way of chemical reaction or by their ability to penetrate not only the dentinal tubules but also the intertubular substance of the surface layer of dentin known as “intertubular bonding”.

Physicochemical aspects: It involves the interfacial attraction between the tooth surface and the adhesive. Each treatment of the dentin leaves it to a specific condition that requires specific polarity and solubility parameters of the ensuing treatment in the bonding procedure. If this requirement is met, the bonding system will possess maximum efficacy (Amussen and Uno, 1992).

Factors affecting adhesion: There must be an intimate contact between tooth structure and restorative materials.

Mechanism of bonding (latest discoveries): The adhesion agents bonds to dentin via the chemical or micromechanical bond. The chemical bond is generated between the intertubular dentin and the primer through the primer’s bifunctional molecules – “intertubular bonding”. The micromechanical bond is obtained through a double mechanism: The bonding agent penetration inside the tubules, where it originates resin tags. Creation of resin – dentine into diffusing area. Called hybrid layer- This area is created by the penetration of liquid resin into the etched dentin, and its thickness will be determined by the relation between the depth of action of the etching acid and the penetration capacity of the resin itself. The action of these two mechanisms i.e. the resin tags, which increases the surface area and hybrid layer, create an excellent tooth restoration junction [9]. The most recent studies carried out by various

schools regarding hybrid layers quality drew attention to three points:

Wet bonding: Early bonding systems were highly hydrophobic and the presence of water on dentin surface was inappropriate. Kanca in 1992 demonstrated that bond could be achieved on moist surfaces too. Water may arise from dentinal tubules, fluid atmospheric water, rinsing procedure etc. Currently available systems are likely to contain hydrophilic resins such as HEMA and are much more tolerant of moisture than their predecessors. Dentin surface must be left moist and not desiccated – which may cause collapse of collagen left intact. Wet bonding has also been shown to improve significantly the marginal seal of restoration in which an acetone based primer is used. However large amount of water on surface may interface with bonding known as “overwet phenomenon”. Acetone containing DBA can tolerate moister surface without much affect on bond strength. Other systems such as containing ethanol e.g. Scotchbond MP require the dentin surface to be blot dried but not desiccate. When acetone containing DBA is applied, acetone primer contacts water, there is increase in its boiling point where as boiling point of water reduces – a process known as “Azeotrophism”. This causes the evaporation of both the acetone and water and the resin is left intact. A wet surface must also be free of contaminants from saliva, blood, GCF etc [10].

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 ^[11].

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:

- 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 diisocyanate. 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.

Disadvantages of 1st generation bonding agents: Hydrolysis of glyco-phosphoric acid dimethacrylate in the oral environment. Difficulty in bulk polymerization of the cyanoacrylates. Instability of NPG-GMA in solution. These factors in combination with very low bond strengths (3 Mpa) prevented the successful clinical use of these bonding agents. The first commercially available agent was (CERVIDENT (Stainless steel white).

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).

Third Generation Bonding Systems: This is the most successful group of dentin bonding agents introduced so far, with increased bond strength and improved clinical performance. This generation DBA requires either removal, modification or dissolution of the smear layer. These agents used a conditioning step on the dentin in conjunction with a bonding agent. The chemistry of these agents is more diverse than 2nd generation systems and includes various agents for conditioning the dentin. This conditioning either modifies or removes the smear layer and subsequently interacts with superficial dentin.

Fourth Generation Bonding System: The fourth generation bonding systems are based on the complete removal of smear layer. It allows the use of both conservative and all etch technique. Also known as universal bonding systems as this bond to dentin, enamel, amalgam, porcelain, composite.

Mechanism of bonding (as proposed by Nakabayashi): ^[12] Diffusion and impregnation of resin into the substrate of partially decalcified dentin followed by polymerization creating a hybrid resin reinforced layer. The hybrid layer formed is an acid resistance mixture of polymerize and tooth structure components creating a resin / dentin composite.

The recently developed fourth and fifth generation of DBA rely on this hybridization as the primary mechanisms for bonding and sealing.

All bond: All bond is a unique development in the field of adhesive dentistry. It is a universal bonding system that will bond composite to all dental related surfaces. Dentin, enamel, metal alloy, amalgam, porcelain and composite. It is also the only system that allows the use of both the conservative and all etch technique.

Mechanism of Bonding: Bonding occur by hybridization. Research by Nakayabashi has shown that strong bond is formed between dentin and resin when a monomer such as 4-META, penetrates the tissue and polymerizes. The resin impregnation creates a transitional "Hybrid layer that is neither resin not tooth, but a hybrid of the two. This direct chemical interaction which the inner tubular dentin is the key to bond strength. All-bond provides a special resin called "Pre-bond" to be used in place of light curing bonding resin when cementing inlays, onlay or crown in order to avoid filling problems while sealing.

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. (One bottle bonding system). These systems rely on the hybridization of dentine for achieving adhesion.

Sixth Generation Dentin Bonding System: Example – Clearfil bond 2 system (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.

Conclusion

The reliability of dentine bonding has improved during 1990s and as a result the number of minimally invasive techniques available to the restorative dentist has increased. It may be anticipated that the effectiveness of adhesive technique to be dentin will improve 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.

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