Fundamentals of enamel and dentin adhesion: Review

Nishant Khurana 1, Kunwar Suhrab Singh2, Radhika Gautam 3, Mahesh Pratap Singh4, Khushboo Mansoori5, Aditya Mishra6

1,5 Post Graduate Student, Dept of Conservative dentistry & Endodontics, PCDS & RC, Bhopal
2 MDS Endodontics, Senior Specialist, Clove dental, New Delhi
3 Maulana Azad Dental College, Associate Dentist Clove Dental
4 Head of the Department, Dept of Conservative dentistry & Endodontics, PCDS & RC, Bhopal
5 Post Graduate Student, Dept of Prosthodontics, PCDS & RC, Bhopal

ABSTRACT

Ever since the demand of esthetics in dentistry has taken front row leaving behind durability as primary focus, enamel and dentin bonding agents have managed to grab enormous attention. Because of this increasing popularity these agents have undergone various stringent in vitro and in vivo studies to assess and exalt its efficacy.

Objectives: the rife literature was reviewed to give more information on bonding agents, including their origin, mode of action, methods of adhesion, and popular systems based on various clinical researches.

Data sources: information from original clinical research papers, review articles, library dissertation, published articles in international journals were added in this review.

Conclusion: pertaining to their adhesive properties, bonding agents have larger in vitro and in vivo success rates. etching is an integral part of adhesion and various factors like complete smear layer removal, concentration, duration and the form in which etchant is used, type of bonding agent applied determine the ultimate success of resin based restorations.

INTRODUCTION

It’s a well-known fact, that the only constant thing is change. Ever since dark ages to current modernised world, humanity has always improved upon pre-existing notions and has always evolved. The field of dental materials has not been exempted from this challenge either, and this is best reflected by the enormous amount evolution seen in dentine bonding agents. In today’s times, the objective of restorative dentistry is vastly different from those of yesteryears and we are breaking the pre-set norms of conventional dentistry. Previously, performance of a restoration was judged based on the concept of longevity, implying that the longer a restoration withstands occlusal forces without succumbing to fracture, the lesser would be the chance for a re-restoration. Therefore, selecting a material with chief function of impeccably withstanding the rigors of the oral environment has been the focus of modern world. Improving the public awareness about tooth-coloured fillings has increased the demand for more aesthetic materials such as composites, glass ionomer cements and porcelain. [1] Of all the innovative materials available in the market today, the resin composites has strengthened itself as the best choice in restorative dentistry. [2]

With the advent of dentine bonding agents, and by exploring its property of adhesion to tooth structure by both micro-mechanical and chemical means, has ushered in a new era in the field of restorative dentistry. [3]
HISTORY
The innovation leading to invention of this material has been rightly attributed to great scientists like Michael Buonocore, Rafel Bowen, Nakabayashi and Fusyama.
Dentin bonding agents have evolved over several generations with its foundation laid by Buonocore who in 1955 introduced etching with phosphoric acid and found that acrylic resin bonds well with etched enamel. The use of phosphoric acid alone was based on the thought that perhaps a simple decalcification resulting in removal of superficial structure was all that was necessary to produce a surface more receptive to adhesion. [4]
Following this Bowen introduced bio-phenol glycidyl methacrylate (BIS-GMA) resin systems 1957. [5] The primary objective of R L Bowen in 1964, investigation was to test the hypothesis that a surface-active Comonomer would give improved water-resistant bonding between a self-curing methacrylate resin and human dentin. He postulated that a coupling agent containing (NPG-GMA) such groups and also groups capable of copolymerization with a dental material should give improved bonding of the material to tooth surfaces. Again Bowen in 1982 suggested that clinically durable adhesive bonding for improving bond strength to dentin and composite resins would improve treatment of cervical erosions, root caries, and other conditions, and would eliminate much of the mechanical cutting of dentin now required for retention of restorations. He concluded that the acidic ferric oxalate solution first dissolves calcium phosphate crystals in the disturbed (smeared) dentin surface layer with a concomitant rise in the PH of the aqueous solution on the surface. [6]
Recent improvements in adhesion based resin systems have created a revolution in dentistry, like the finding of hybrid layer by Nakabayashi in 1982 and introduction of one bottle adhesives by Ferrari et al in 1997. Therefore, clinicians have had to rise to the challenge of confronting this continuous and rapid change and had to accept the same.
N. Nakabayashi et al in 1996 studied bonding to intact dentin and reported that the presence of a smear layer on dentinal substrates can compromise bonding. They stated that smear layers are removed by acidic agents that selectively extract calcium salts from dentin surfaces to leave a collagen-rich substrate. Acid-conditioned dentin (i.e., demineralized) is then primed and an adhesive agent applied.
After these primary researchers many studies took place with advent of new bonding agents with the principle goal of durable adhesive dentistry.

FUNDAMENTALS OF ENAMEL AND DENTIN ADHESION
The word adhesion is from the Latin word adherer, which means ad-to and hearer- to stick. Adhesion refers to the attraction between the atoms and molecules at the contacting surface of different materials (de brayer et al 1951, wake 1982).
In adhesive terminology adhesion or bonding is the attachment of one substrate to another. The surface of the substrate that is adhered to is termed as adherent.
The adhesive or bonding agent may be defined as the material that when applied to the surface of the substrate can help in joining them together at the micro level, resist separation and transfer loads across the bond.
An essential requirement for any of this phenomenon to take place is that the two materials being joined together must be sufficiently close and intimate in contact and besides this sufficient wetting only occurs if the surface energy of adhesive is less than the surface energy of the adherent. If the adhesive has a high surface tension, then it would form a droplet which will prevent adhesion. Based on this theory of wetting and surface free energies, adhesion to enamel is easier to achieve than adhesion to dentin. This is because enamel is made up of hydroxyapatite which has a high surface free energy whereas dentin has a low surface free energy because it is composed of two different materials hydroxyapatite and collagen. Therefore, achieving a substantial wetting is easy for enamel than for dentin. The natural tooth surface should be thoroughly cleaned and penetrated prior to bonding procedures to increase the surface free energy.

**TYPES OF ADHESION**

Van Noort in 1994 suggested that one or more of the following mechanisms can create an adhesive bond:

- Mechanical Adhesion
- Physical Adhesion
- Chemical Adhesion
- Adhesion through Molecular Entanglement

**MECHANICAL ADHESION**

Here, retention is by the interlocking of one phase into the micro-surface of another. This type of adhesion can be due to following effects:

**A. GEOMETRICAL EFFECTS**

These are caused by microscopic porosity or roughness of the surface, i.e. mechanical locking provided by undercuts and grooves within the surface etc.

**B. RHEOLOGICAL EFFECTS**

This is caused by flow of materials in both liquid and semisolid phase. Mechanical adhesion which is also known as micro-mechanical adhesion results from the presence of surface irregularities that give rise to microscopic undercuts. The liquid adhesive penetrates these undercuts and gets locked within them. A prerequisite for this form of adhesion is that the adhesive can readily flow and adapt to the surface of the substrate.
PHYSICAL ADHESION

When two surfaces are in close proximity to each other, secondary forces of attraction are developed through dipole-dipole interactions. The polar reaction occurs because of attractive forces between the differently charged molecules. The magnitude of this energy is dependent upon the alignment of the dipoles. This type of bonding leads to a rapid bond which is also reversible in nature, because the molecules remain chemically intact on the surface as long as they are in close proximity. Therefore, this weak physical adsorption is also easily overcome by thermal energy which causes expansion and is not suitable if a permanent bond is desired.

CHEMICAL ADHESION

If an absorbed molecule dissociates on contact with a surface and constituents alone rearranges themselves in such a way that as for covalent, a strong adhesive bond can result, then this form of adhesion is called as chemi-sorption. The feature that differentiates the chemical bond from the physical type of bond described previously is that a chemical reaction takes place between the molecules of the substrate. Adhesives must be strongly attracted chemically to the surface of substrate to form strong bond and also require identical reactive groups on both surface.

ADHESION THROUGH MOLECULAR ENTANGLEMENT

So far it has been thought that there is a distance between the surfaces of the adhesive and the substrate, in effect, the adhesive is actually adsorbed on the surface and becomes surface active. If the substrate is permeable the adhesive is able to penetrate through the surface of the substrate and absorb itself into the substrate rather than getting adsorbed just onto the superficial surface of the substrate. If the absorbing molecule is a long chain molecule it forms polymers in the pre-treated layer,
the resultant enlargement between the adhesive and the substrate is capable of producing very high bond strength. This approach is being adopted for resin bonding system. [7]

**ENAMEL ACID-ETCHING TECHNIQUE**

Adhesion to enamel is achieved through acid etching of this highly mineralized substrate, which substantially enlarges its surface area for bonding. This enamel—bonding technique, known as the acid—etching technique, was the invention of Buonocore in 1955. [8] He demonstrated a 100-fold increase in retention of small buttons of polymethylmethacrylate to incisors in vivo when enamel was etched with 85% phosphoric acid for 2 minutes. Further research into the underlying mechanism of the bond suggested that tag like resin extensions were formed and micromechanically interlocked with the enamel micro porosities created by etching.

Enamel etching transforms the smooth enamel surface into an irregular surface with a high surface-free energy (about 72 dynes/cm), more than twice that of un-etched enamel. [9] An unfilled liquid acrylic resin with low viscosity, the enamel bonding agent, wets the high-energy surface and is drawn into the micro porosities by capillary attraction. [10]

Enamel bonding agents are commonly based on Bis-gma, developed by Bowen in 1962 [11] or urethane Dimethacrylate (UDMA). Both monomers are viscous and hydrophobic and are often diluted with other monomers of higher hydrophilicity and lower viscosity, such as Triethylene glycol dimethacrylate (TEG-DMA) and HEMA. [12] The bond between enamel and the restorative material is established by polymerization of monomers inside the micro porosities and by copolymerization of remaining carbon-carbon double bonds with the matrix phase of the resin composite, producing strong chemical bonds. [13]

In addition, the potential for chemical interaction between specific monomers and the etched enamel surface cannot be excluded. [14] Acid etching removes about 10 um of the enamel surface and creates a micro porous layer from 5 to 50 um deep. Three enamel-etching patterns have been described. These include type I, in which there is predominant dissolution of the prism cores; type II, in which there is predominant dissolution of the prism peripheries; and type III, [15]

Macro tags are formed circularly between enamel prism peripheries; micro-tags are formed at the cores of enamel prisms, where the monomer cures into a multitude of individual crypts formed where hydroxyapatite crystals have dissolved. Micro tags probably contribute most to the bond strength because of their greater quantity and large surface area. [16]

**PHOSPHORIC ACID ETCHANTS**

Generally, use of a phosphoric acid concentration between 30% and 40%, an etching time of not less than 15 seconds, and washing times of 5 to 10 seconds are recommended to achieve the most receptive enamel surface for bonding. [17] Historically, some controversy existed about the concentration of phosphoric acid that would provide optimal etching efficacy, because some acids have been reported to form precipitates on the surface that might interfere with resin bonding. [18] One study showed that 50% phosphoric acid applied for 60 seconds on enamel produces a precipitate of
Monocalcium phosphate monohydrate that can be rinsed off. A precipitate of Dicalcium phosphate dehydrates produced by etching with a less than 27% phosphoric acid was found not to be easily removable. [19]

An acid gel is generally preferred over a liquid because its application is easier to control. In vitro bond strengths of resin composite to phosphoric Acid etched enamel typically average 20 MPA. This bond strength is thought to be sufficient to resist the shrinkage stress that accompanies the polymerization of resin composites. [20]

Also, if the preparation is completely bordered by enamel, acid etching significantly reduces micro leakage at the cavosurface interface. This enamel etching technique has proven to be a durable and reliable clinical procedure for routine applications in modern restorative dentistry. [21]

The etching time has also been reduced from the traditional 60-second application with 30% to 40% phosphoric acid to etching times as brief as 15 seconds. Several laboratory and clinical studies have demonstrated bonding effectiveness to be equivalent with etching times from 15 to 60 seconds. Adequate rinsing is an essential step. Rinsing times of 1 to 3 seconds on flat surfaces have been shown to provide for adequate bond and seal. For preparations with more geometric form, a rinse time of 5 to 10 seconds is recommended. The use of ethanol to remove residual water from the etched pattern has been reported to enhance the ability of resin monomers to penetrate the etched enamel surface irregularities. [22]

In addition to phosphoric acid, other inorganic and organic acids have been advocated for acid etching enamel (and dentin), as they were supplied with specific commercial adhesives.

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