

Bonding Agents in Dentistry and Recent Advances

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Abstract

Introduction: The main aim of restorative dentistry is to restore the tooth tissue in its proper form, function, aesthetics as well as maintaining physiologic integrity in harmony with surrounding soft and hard tissues. Since many of the restorative materials do not adhere to dental tissues like enamel and dentin due to different physical and chemical properties, which lead to microleakage at tooth restoration interface, thus bonding agents play an essential role in restorative dentistry. Bonding agents have evolved through different generations in the last few decades, along with some recent advances that are changing the entire restorative procedure. The bonding agents evolved in terms of chemistry, several bottles, mechanism of action, the technique of application, and as well as its clinical implication. The most widespread is self-etching primer, which has been used for more than a decade, whereas all-in-one adhesives came into consideration for the past two years. With the development of this system, it has significantly simplified resin bonding since a separate etching step is no longer requires, thereby saving time. .

Aim of the Study: The purpose of the review is to understand the different generation of bonding agents and newer modification for better adhesive properties.

Methodology: The review is a comprehensive research of PUBMED since the year 1952 to 2019.

Conclusion: Dentin bonding is one challenging concept in clinical practice due to an increase in demand for aesthetic restorative treatments. It lead to recent advances in dentistry and more development of adhesive material used in adhesive systems and composites, as well as the techniques used in restoring the teeth to give it a natural tooth appearance. With the advent of acid etching into clinical practice, many bonding agents are developed until this date to improve the quality of adhesives and composite restorations. The manufactures are progressing more in the development of a new adhesives system to simplify the process and improve results in terms of stability and bond strength, further leading to a more durable resin bond.

Keywords: Dentin Bonding Agents; Classification; Swear Layer; Hybrid Layer; New Modification

Background and Evolution

In 1949, Dr. Hagger was the first person to patent “Cavity Seal,” a material to be used in combination with “Sevriton” (chemically curing resin). This contained glycerol phosphoric acid dimethacrylate as an adhesive polymerized by initiator sulfonic acid. It is based on the acidic monomers capable of etching and interacting on a molecular level to form a physical and chemical bond between the tooth and restoration. Many others soon adopted this concept, and different generations of adhesive material evolved later on by the formation of an interface of what is called the “Hybrid layer” at present [1,2].

Buonocore, in 1955, experimented on adhesion to enamel through acid etching using 85% of phosphoric acid to alter enamel surface, making it suitable for bonding with resin and improve retention of a restoration. Matsui and Gwinnett described the effect of phosphoric acid on enamel surface in the form of “prism-like” tags or now commonly called resin tags, which was otherwise not seen in unconditioned enamel [3].

The enamel bonding turned out to be micromechanical, while the same concept was hard to apply on dentin due to the use of hydrophobic resins. In 1970, Eick explained the idea of the smear layer as the main obstacle to dentin adhesion using a scanning electron microscope. In 1982, Nakabayashi told the formation of the hybrid layer, which is still presently described as a primary mechanism of adhesion through bonding agents. He stated that resin could infiltrate into acid-etched dentin to form a new structure that resin-matrix reinforced by collagen fibrils [4-6].

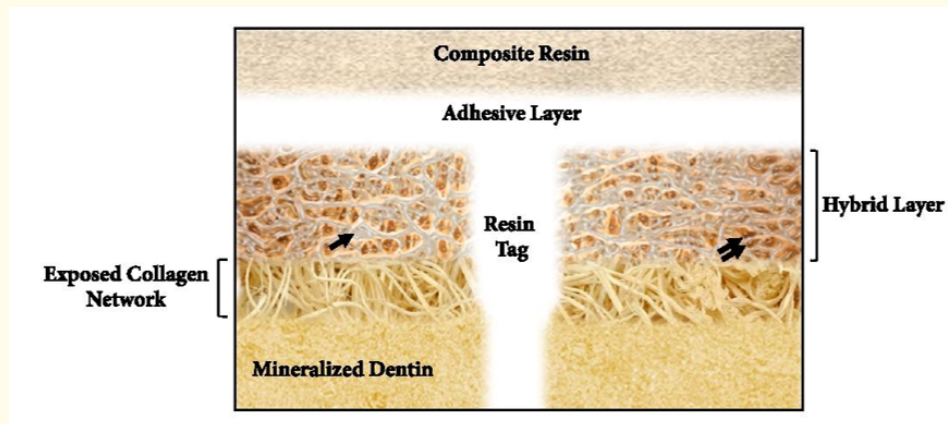


Figure 1: Showing the formation of a hybrid layer and resin tag in the collagen network of dentin for the resin to flow into [7].

The three-step total-etch adhesive system was introduced in the early 1990s, which included an etching of dentin with phosphoric acid, and the etchant is rinsed off, followed by the application of hydrophilic primers before applying hydrophobic resin to complete hybridization [8].

Mechanism of action and composition of dental tissues

With the development of these adhesive materials, there has been a revolution in terms of restorative and preventive dentistry. The process of cavity preparation has majorly changed with no more prolonged need to provide mechanical retention through dovetails, undercuts, grooves, and pins. In this way, the adhesive system is proven to be conserving a large amount of sound tooth structure as well as preventing secondary caries caused by microleakage [9].

The adhesive system is composed of monomer, which contains both hydrophobic and hydrophilic groups. The hydrophobic group is responsible for co-polymerization with restorative material, and the hydrophilic group increases the wettability to hard dental tissues. Chemically, adhesives are composed of initiators, inhibitors or stabilizers, solvents, and inorganics fillers. The influence of adhesive bonds depends on the anatomy of the tooth and composition of enamel and dentine [10].

The enamel is made up of hard crystalline structure hydroxyapatite (HAp) with stronger intermolecular forces and high energy surface while dentin is a composite of HAp covering collagen network. It's humid, less hard than enamel, with low intermolecular forces and low energy surface. The structure of dentin is different from enamel, and therefore the bonding in dentin is more complicated. It has organic content, smear layer, and dentinal tubules inside, the density of which varies with dentinal depth and water content of dentin, lowest in superficial dentin, and more in deep dentin. The superficial dentin contains less number of tubules, the intertubular permeability of resin is responsible for bond strength here while in deep dentin, dentinal tubules are more and the permeation of resin into intratubular dentin will provide higher bond strength. Unlike enamel, dentin cannot be dried quickly, so the process of bonding in dentin is different than that of enamel [11].

Bond strength depends on the composition of the tooth structure, as given in the table 1 [8].

Components	Enamel	Dentine
Inorganic phase (HAp) %	94-96	50 - 70
Calcium phosphate ratio	1.64	1.56
Organic Phase (Collagen)%	4 - 5	20 - 30
Water %	1 - 4	10 - 20

Table 1

The difference between hydrophilic and hydrophobic adhesives is the chemical composition of their monomers solvents. Most of the adhesives use hydroxyethyl methacrylate (HEMA) and Bisphenol glycidyl methacrylate (bis- GMA). HEMA is more miscible in Water thus serves as a good polymerizable wetting agent in adhesives while bis-GMA is more hydrophobic and will absorb only 3% of Water [12].

Smear layer

A smear layer is formed by cavity preparation that alters the uppermost layer of the tooth and covers the tooth surface forming 1.0 µm layer of cutting debris. These debris tags obstruct the orifice of dentinal tubules, and it can extend up to a depth of 1 - 10 mm into dentinal tubules known as smear plugs, which are contiguous with smear layer and mostly contain crushed and shattered hydroxyapatite,

denatured and fragmented collagen. In clinical practice, the smear layer, which has a composition of cut dental tissues contaminated by bacteria and saliva, serves as a true barrier and reduces dental permeability. To overcome this problem, etching is required before bonding to the dentin surface to increase bond strength and durability of the restoration. The smear layer can either be removed by etch-rinse procedure or dissolved using phosphoric acid in case of a total-etch adhesive system. When a self-etching system is used, different acidic primer is used to either modify, disrupt, or completely solubilize smear layer [13].

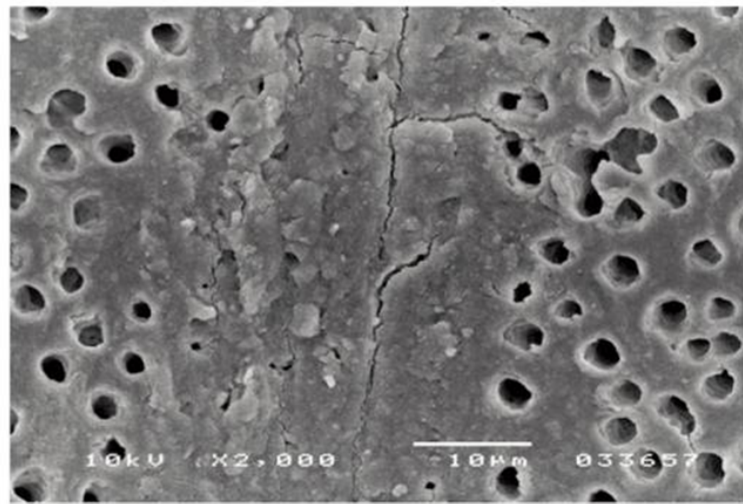


Figure 2: A scanned electron microscope shows a micrograph of the smear layer [8].

Classification of adhesives by generation

Because of the complexity of bonding agents used in many decades, the concept of generation was used to have a classification that refers to when and what type of adhesive was developed. The adhesive system began in 1955 by Buonocore, with changing concept, adhesives have evolved from no-etch to total-etch that is 4th and 5th generation to a self-etch system that is 6th, 7th and 8th generation as shown in the table 2 below, with each generation the number of bottles is reduced and so as the procedural steps [5,8].

Generation	Number of Steps	Surface pre-treatment	Components	Shear bond strength (MPa)
1 st	2	Enamel etch	2	2
2 nd	2	Enamel etch	2	5
3 rd	3	Dentine conditioning	2 - 3	12 - 15
4 th	3	Total etch	3	25
5 th	2	Total etch	2	25
6 th	1	Self-etch adhesive	2	20
7 th	1	Self-etch adhesive	1	25
8 th	1	Self-etch adhesive	1	Over 30

Table 2: Classification of adhesives by generation [8].

First generation

The first generation was developed in the 1960s. Buonocore stated that Glycerophosphoric Acid Dimethacrylate (GPDM) can bond to dentin etched with hydrochloric acid. However, the bond strength from this adhesive technique was found below. N-phenyl glycine glycidyl methacrylate (NPG-GMA) used as Cervident was the first commercially available dentin bonding agent. They bond with calcium with the process of chelation, but the difficulty in the bulk of polymerization, instability of NPG-GMA in solution leads to low bond strength (1 - 3 MPa), and ultimately the failure of these bonding agents [14,15].

Second generation

The second-generation bonding agents were developed in the 1970s and 1980s. The use of second-generation leave the smear layer on a large basis if not whole and produced variable results but better than first-generation in terms of bond strength (5-6 MPa). Ethyl methacrylate, Phosphate ester, Polyurethane were incorporated in them and commercially available as Bondlite, Prisma universal bond, Creation Bond, Scotch bond. The major disadvantage was still a low bond strength, poor wetting, and hydrolysis in the oral environment leading to failure of the restoration [15,16].

Third generation

The third generation bonding agent does not remove the whole smear layer but modifies it before the application of the dentin bonding agent. In this system, dentin is etched with an aqueous solution of 10% citric acid and 3% ferric chloride, followed by application of 35% HEMA and a self-curing adhesive resin containing 4-META, MMA, and tri n-butyl borane (TBB), which acts as a polymerization initiator. In this way, the third generation of bonding agent system consists of a conditioner, primer, and bonding agent. The commercially available adhesive system of the third generation is C&B metabond (Sun Medical), Super-bond D-Liner, and Amalgam bond plus (Parkell) [17].

Fourth generation

The more enhanced adhesive capacity leads to the improved clinical effectiveness of the fourth-generation adhesive system which includes pre-treatment of dentin with primers or conditioner that makes heterogenous and hydrophilic dentinal substrate more receptive to bonding. The fourth generation is adhesives are generally referred to as three-step etch and rinse adhesive comes with 30 - 40% phosphoric gel. This total-etch technique allows the etching of both enamel and dentin simultaneously by using phosphoric acid for 15 - 30 seconds. The surface is left moist to prevent collagen collapse. Fourth-generation is used for cavities of enamel and dentin, and bonding to substrate such as porcelain and alloys. Commercially available adhesives in this generation are All-bond 2, Optibond FL, Permaqui (Ultra dent), and Scotch bond Multipurpose, etc [15].

Fifth generation

Because of the more complex system of fourth-generation with more number of steps involved, researchers worked on developing simpler adhesive systems. This includes etching of enamel and dentin simultaneously with 35 - 37% of phosphoric acid for 15 - 20 seconds followed by the application of primer and bonding agent present in one bottle with the general composition of HEMA, Bis-GMA, dimethacrylate, patented polyalkenes acid copolymer, Water and ethanol. However, this generation requires fewer steps, but the proper-



Figure 3: Showing different Bonding adhesive system.[8]

ties are inferior to the fourth generation. The commercially available fifth-generation bonding agents are excited (Ivoclar Vivadent), One-step (several versions, Bisco), OptiBond Solo (several versions, Kerr), Prime, and Bond (several Versions, Dentsply), and Single Bond or Scotchbond 1 (several versions) [18].

Sixth generation

Due to further demand for simplification and fewer clinical steps, the sixth generation was evolved, which consists of self-etch adhesives. It omits the separate conditioning phase and is composed of two different solutions. This contains two-step self-etch adhesive and one step two-component self-etch adhesives. Commercially available adhesives include AdheSE, clearfil SE Bond, and clearfil Protech Bond, OptiBond Solo Plus [16].

Seventh generation

The seventh and the latest generation of adhesives consist of a single component that is one-step self-etch adhesives. It combines all the steps of conditioning, priming, and application adhesive and does not require mixing unlike in the sixth generation. Even though the steps are fewer but the bond strength of the seventh generation is found to be lower than that of fourth and fifth-generation adhesives. Commercially available agents are Clearfil S Bond (Kuraray), G-Bond (GC), i-Bond, and Xeno IV (Dentsply) [15].

Eighth generation

To overcome the shortcoming of lower bond strength, the eighth generation incorporated nanosized fillers. The addition of the nanofillers with particle size 12nm can increase the penetration of resin monomers and hybrid layer thickness, this in turn, improves the mechanical properties of the bonding system. These nano bonding agents are the solution of nano-fillers that provide better bond strength, longer shelf life, and stress absorption to restoration, affect the adhesive viscosity and penetration ability of resin monomers into collagen fiber space [8].

Advances and methods to modify bonding system

Adhesive material with anti-matrix metalloproteinase functions

On the application of MMPs inhibitors as components of the adhesive system, a bond system is provided with improved durability of the adhesive restoration. Such adhesives have properties to decrease the collagen degradation of collagen fibrils within the hybrid layer by inhibiting host-derived collagen lytic activity [19].

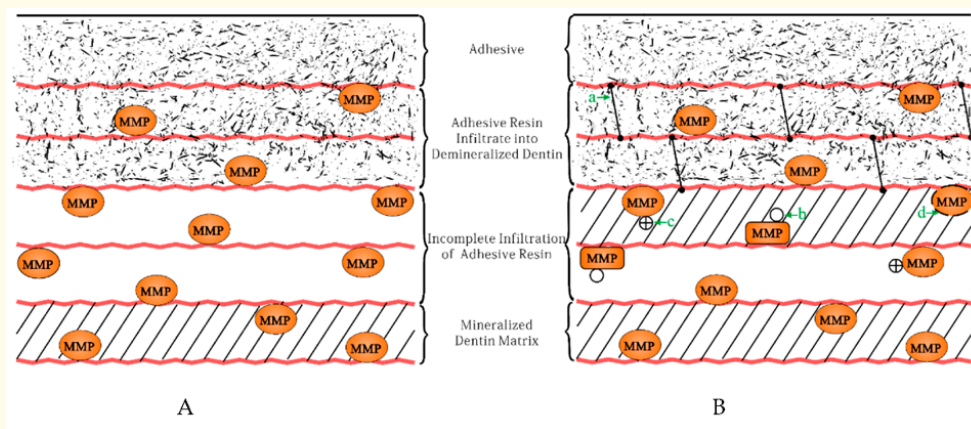


Figure 4: Showing A: Common condition of resin-dentin bonding. B: The different ways of inhibiting MMPs. a) cross-linking of collagen. b) changing the conformation of MMPs. c) Electrostatically binding to the catalytic site of MMPs. d) Entrapping MMPs to collagen in newly formed crystal [19].

Adhesive with remineralization function

The adhesive system with a capacity of remineralization is believed to increase the longevity of adhesive restoration using healing microcracks and to neutralize acidic acids in adhesive joints. The possible cause of demineralization is low pH; therefore, to combat demineralization pH should be raised by providing alkaline ions like Ca and P to neutralize acids. The commercially available fluoride-releasing adhesive such as (OptiBond Solo and Reactmer Bond) showed a reparative ability in bond leakage by inducing crystal growth within gaps of resin dentin interfaces. Apart from this bioactive glass, calcium phosphate and hydroxyapatite can be used as a good source of CaP for remineralization [19].

Antibacterial bonding system

The addition of antibacterial primer can help to kill residual bacteria in the tooth cavity; thus, antibacterial bonding agents can combat the issue of biofilms and recurrent caries at tooth and composite interface. Ag ions interact with vital enzymes of bacteria and inactivate them cause the DNA in bacteria to lose their ability to replicate and, ultimately, cell death. Thus, the addition of nanoparticles of silver can have a high surface area; lower filler level can provide adequate antibacterial effects without affecting the color of restoration and mechanical properties of dental adhesives [19].

Combining different agents

The concept of combining different agents in the bonding system is to get multiple desirable functions in one system and hence improve the durability of resin-dentin bond. A series of work is done to improve the bonding system with multiple agents such addition of quaternary ammonium dimethacrylate (QADM) and nanoparticles of silver (NAg) into the bond of SBMP, combining QADM with NAg, Dimethylaminododecyl methacrylate (DMADDM) with NAg and NACP to modify the primer of SBMP(Scotch bond Multi-Purpose), incorporating DMADDM and NAg into primer and bond of the same bonding agent to enhance antibacterial potency of bonding system without significantly affecting dentin bond strength [19].

Conclusion

The dentin bonding agents with different generations can be used before luting of cast ceramic or composite restoration with resin cement when dentin is exposed since it increases the bond strength, reduced microleakage, post-treatment sensitivity. In this way, the Adhesive bonding system has created a new era in the field of dentistry by its property of adhering to the tooth structure, utilizing both micromechanical and chemical means. The new adhesive system also eliminates above-stated problems, thus increases the bond strength and longevity of the restoration.

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