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**REVIEW ARTICLE**

# DENTIN BONDING AGENTS -A REVIEW

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## ABSTRACT

**Adhesive dentistry has undergone great progress in the last decades. There have been changes in chemistry, mechanism, number of bottles, application technique, and clinical effectiveness. The first, second and third generations are classified under historical title while; etch&rinse, self-etch and multi-mode adhesives are classified under the title of current clinical practice procedures strategies. The preferred properties of adhesive systems are biocompatibility with dental tissues, improved bond strength to dental tissues, and better resistance to chewing stresses. In recent years, the success rate of restorative treatment of teeth that have suffered from caries or loss of supporting tissue has increased considerably due to the developments in dentin donding systems.**

**Keywords: Dental enamel, dentin, dentin-bonding agents, dental adhesives, classification**

## INTRODUCTION

Adhesive resins are designed to provide strong coupling between resin composites and enamel and dentin. The earliest dental adhesives were relatively hydrophobic and were placed directly on enamel and dentin smear layers although the presence of these layers were unknown at that time [1].

Dental adhesives are solutions of resin monomers that make the resin dental substrate interaction achievable[2]. Adhesive systems are composed of monomers with both hydrophilic groups and hydrophobic groups. The former enhance wettability to the dental hard tissues, while the latter allow the interaction and co-polymerization with the restorative material[3]. The chemical composition of adhesives also includes curing initiators, inhibitors or stabilizers, solvents and, in some cases, inorganic fillers [3].

Adhesion to dental substrates starts with an acid-etching step, which means that enamel or dentin undergoes surface demineralization. For enamel, the prisms that form its highly-mineralized structure would be selectively removed, leaving a porous/microretentive surface favorable to resin infiltration,which in turn results in stable resin-enamel bonds [4]. On the other hand, dentinpossesses a more complex composition (organic/inorganic content) and a heterogeneous morphology when compared with enamel, therefore acid etching would not only produce microretentions if applied to dentin but would also result in the exposure of collagen fibrils [2, 4]. This event activates bound matrixmetalloproteinases (MMPs)-2, −3, −8,

−9, and −20, and cysteine cathepsins (CCs), which will slowly degrade the collagen fibrils [5–9], making it difficult to achieve stable resin-dentin bonds.
Several studies have investigated the degradation mechanism of dental adhesive interfaces [2-4]. Collectively, it seems that to eliminate collagen degradation, any denuded collagen fibril that originated during acid etching should be completely protected with resin monomers, thus preventing activation of MMPs and CCs. Even for self-etching adhesives in which surface demineralization and resin infiltration occur simultaneously, collagen degradation would be an unavoidable process due to incomplete collagen protection by monomers. It is worth mentioning that bonding with most of theadhesive systems available today usually results in partially infiltrated collagen fibrils, thus favoring degradation.

## CLASSIFICATION OF DENTIN ADHESIVES

Dentin adhesives can be classified in three main groups[10-13].
Chronological classification

### 1. HISTORICAL CLASSIFICATION

First generation
Second generation
Third generation

### 2. CLASSIFICATION ACCORDING TO THEIR EFFECT ON SMEAR LAYER

-Smear tabakasınınüzerineuygulanan
-Modifying the smear layer
-Completely removes the smear layer
-Dissolves the smear layer

### 3. CURRENT CLASSIFICATION (ACCORDING TO CLINICAL APPLICATION TYPES)

Etch&rinse (ER) adhesives
Three-stage etch & rinse (ER) adhesives (Fourth generation)
Two-stage etch & rinse (ER) adhesives (Fifth generation)Self-etch adezivler
Two-component self-etch adhesives (Sixth generation)
One-component and one-stage self-etch adhesives (All-in-one)
Eighth generation
Universal (Multi-mode)
The first group is called the historical classification. It consists of 1st., 2. and 3. generation dentin adhesive systems.
Second group: Dentin adhesives are classified according to their effect on the smear layer. They can be examined in 4 groups: The adhesive systems which are applied on the smear layer, modify the smear layer, remove the smear layer completely and dissolve the smear layer [13].
The third group is the current classification, in other words, the classification of dentin adhesives according to the type of application in the clinic:
1. Etch&rinse (ER)
a-3-stage
b-2-stage
1. Self-etch
a-2) Stage
b-1) Stage
Universal (Multi-mode) [14].

**FIRST GENERATION**

The first generation dentin bonding agents were developed in the early 1960's 15. Buonocore., et al. in 1956 reported that GlycerophosphoricAcid Dimethacrylate (GPDM) could bond to hydrochloricacid-etched dentin surfaces However, the bond strengths todentin attained with this primitive adhesive technique were only 1to 3 MPa 15.

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 16.dentin bondings in this generation had a hydrophobic structure, so their attachment strength to dental tissues was low (2-6 MPa) [17].

**SECOND GENERATION**

The second generation of dentin bonding agents were introduced in the late 1970s, and sought to improve the coupling agents that were utilized in the first generation of adhesives. The 2nd generation of dentin adhesives primarily used polymerizable phosphates added to bis-GMA resins to promote bonding to the calcium in mineralized tooth structure [18,19]. Bonding mechanism involves formation of ionic bond between calcium and chlorophosphate groups. This ionic bond would rapidly degrade in water submersion (again analogous to saliva) and even the water within the dentin itself, and cause debonding and/or micoleakage[18]. The smear layer was still not removed, and this contributed to the relatively weak and unreliable bond strengths of this second generation [18]. The smear layer is really a smooth layer of inorganic debris that remains on the prepared dentin surface as a result of tooth preparation with rotary instruments(the drill). This generation of bonding agents is no longer used, due mainly to failed attempts to bond with a loosely bond smear layer. Bond strength: 4-6 Mpa[20].

**THIRD GENERATION**

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[21].Thus the third generation bonding agent came out with a system

consisting of Conditioner, Primer and Bonding agent. Thispaved the way for the further development in bonding agents.

**FOURTH GENERATION**

In 1980s and 1990s, fourth generation dentin bonding agents were introduced. The fourth generation materials was the first to achieved complete removal of smear layer [22] and still considered as the golden standard in dentin bonding. In this generation, the three primary components (etchant, primer and bonding) are typically packaged in separate containers and applied sequentially. The concept of total-etch technique and moist dentinal hallmarks of the 4th generation systems [22, 23], where dentin and enamelare etched at the same time with phosphoric acid (H3PO3) for a period of 15-20 s [24]. However, the surface must be left moist "wet bonding", in order to avoid collagen collapse. The application of a hydrophilic primer solution can infiltrate the exposed collagen network forming the hybrid layer[22, 25]. The hybrid layer is formed by the resin infiltrated surface layer on dentin and enamel. The goal of ideal hybridization is to give high bond strengths and a dentin seal [26]. Bond strengths for these adhesives were in the low- to mid-20 MPa range and significantly reduced margin leakage compared to earlier systems [27].

## FIFTH-GENERATION

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 interms of their bond strength [28].

## SIXTH GENERATION

The sixth generation bonding systems sought to eliminate the etching step, or to include it chemically in one of the other steps: (self-etching primer + adhesive) acidic primer applied to tooth first, followed by adhesive or (self-etching adhesive) two bottles or unit dose containing acidic primer and adhesive; a drop of each liquid is mixed and applied to the tooth. It is recommended that the components are mixed together immediately before use. The mixture of hydrophilic and hydrophobic resin components is then applied to the tooth substrate [29]. Evidently, these bonding systems are characterized by the possibility of achieving a proper bond to enamel and dentin using only one solution [22]. The biggest advantage of the sixth generation is that their efficacy appears to be less dependent on the hydration state of the dentin than the total-etch systems [25].

## SEVENTH GENERATION

The seventh generation or one-bottle self-etching system represents the latest simplification of adhesive systems. With these systems, all the ingredients required for bonding are placed in and delivered from a single bottle[30].

Whereas there is a mixing process prior to application in type 1 single-stage adhesive systems with two-components,the mixing process is not necessary in type 2 single-stage (all-in-one) adhesive systems with one component [32]. Compared to classical adhesive systems, single-stage adhesive systems contain non-polymerized ionic monomers that come in direct contact with the composite [33].This unreacted acidic monomers are partly responsible for the mismatch between single-stage adhesive systems with self-cure composites [33]. Furthermore, these systems tend to act as semi-permeable membranes [32]resulting in hydrolytic degradation of the resin-dentin interface [34]. These adhesives usually contain resin monomers with organophosphate and carboxylate structure, as they have to have sufficient acidity to demineralize the enamel and dissolve the smear layer [35]. They also contain highly acidic hydrophilic monomers and water (5 to 50%) which allows acidic monomers to be ionized.However, due to their content, they are prone to hydrolysis, hydrolytic degradation and chemical degradation [34,35].

## EIGHTH GENERATION

In 2010, voco America introduced vocofuturabondDC as 8th generation bonding agent, which containsnanosized fillers [36,60]. In the new agents, the additionof nano-fillers with an average particle size of 12 nmincreases the penetration of resin monomers and thehybrid layer thickness, which in turn improves the mechanicalproperties of the bonding systems[37, 38].Nano-bonding agents are solutions of nano-fillers which produce better enamel and dentin bondstrength, stress absorption, and longer shelf life [40,59]. These new agent from self-etch generations have an acidic hydrophilic monomers and can be easily used on the etched enamel after contamination with saliva or moisture[39,58]. Based on the manufacturer, nano-particles acting as crosslinks, will reduced the dimensional changes [37,38]. The type of nano-

fillers and the method that these particles are incorporated affect the adhesive viscosity and penetration ability of the resin monomers into collagen fibers spaces [38,57]. Nano-fillers, with dimensions larger than 15-20 nm or a content of more than 1.0 percent by weight, both can increase the viscosity of the adhesives, and may cause accumulation of the fillers over the top of the moistured surface. These clusters can act as flaws which may induce cracks and cause a decrease in the bond strength [38,56].

## ETCH AND RINSE

The three-steps total-etch adhesive systems were introduced in early 1990s [46,55], that involve acid etching, priming and application of a separate adhesive. Each of the three-steps can accomplish multiple tasks ending with sealing the bonded interface with a relatively hydrophobic adhesive layer. Consequentially, an inter-diffusion layer is formed that called hybrid layer. Etch-and-rinse adhesives are characterized by an initial etching step, followed by a compulsory rinsing procedure which is responsible for the complete removal of smear layer and smear plugs. On enamel, acid-etching selectively dissolves the enamel rods,creating macro-and micro porosities which are readilypenetrated, even by ordinary hydrophobic bonding agents, by capillary attraction [47,53]. Upon polymerization, this micromechanical interlocking of tiny resin tags within the acid-etched enamel surface still provides the best achievable bond to the dental substrate [48,54]. Dentin adhesion is more challenging than enamel adhesion due to dentin composition, rendering the etch-and-rinse strategy a highly sensitive technique [49,52]. Concurrently, acid-etching promotes dentinedemineralization over a depth of 3-5 lm, thereby exposing a scaffold of collagen fibrils that is nearly totally depleted of hydroxyapatite[50,51].

## UNIVERSAL ADHESIVE SYSTEMS

Universal adhesives have been used in clinics since 2011. These systems are also known as multi-mode or multi-purpose adhesives. Because these adhesive systems can be used as SE adhesives, the ER adhesives or SE adhesives in dentin tissue and ER adhesives on enamel tissue (a technique known as selective acidification of enamel ) [41,57]. These systems, enabling the implementation of the total-etch or selective-etch approaches, have been developed to improve weakness of the previous generation single-step SE adhesives and to obtain a strong bonding in enamel tissue[41,42,58]. Its composition is an important factor to be taken account, since most of these adhesive contain specific carboxylate and/or phosphatemonomers that bond ionically to calcium found in hydroxyapatite (Ca10[PO4]6[OH]2) [43,44,59], that could be influence the bonding effectiveness [45,60].

## CONCLUSION

Safe bonding of composite resins to enamel and dentin tissues via adhesive systems allows more conservative cavity preparation instead of cavity prepared for amalgam restorations in operative dentistry. Advances in dentin bonding systems and application techniques make it possible for these systems to be used in many other areas of Dentistry. However, even if better and easier-to-use materials are produced, the clinician must first pay attention to the technique during the application in order to make a successful restoration in the clinic. However, it is also very important that bonding is done under ideal conditions.

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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