

## Overview of Dental Adhesive Systems

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### Abstract

**Introduction:** Restorative dentistry cannot be accomplished without the use of a dental adhesive system. Dental adhesives not only provide bonding in cases of resin restoration but also provide retention in a wide range of indirect restoration like inlay, onlay, veneers, and ceramic crowns. The adhesive system in dentistry is used in various procedures like during application of pit and fissure sealants, obturation using resin-based obturation materials, treatment of dental hypersensitivity, and adhesion of orthodontic brackets. Advances in dental adhesive systems help in the advancement of modern restorative dentistry. Adhesive Dentistry helps in the conservation of tooth structure, restoration using a tooth-colored resin material, and ceramic crown uses the concept of dental adhesion and reduces the amount of tooth structure compromised in the conventional cavity and tooth preparation.

**Aim of Work:** This review aims to assess the knowledge about current adhesive systems used in clinics.

**Methodology:** This review is a comprehensive research of PUBMED and ResearchGate from the year 1968 to 2019.

**Conclusion:** During the current rage of conservative dentistry, dental adhesives have a massive role in the preservation of tooth structure. Apart from that, this leads to restoration using resin bonded tooth-colored materials, thereby enhancing the esthetics of dental restorative procedures. This review is an accumulation of all the classifications and mechanisms of the dental adhesive system available in the present era.

**Keywords:** Dental Adhesive System; Adhesion Decalcification; Hybrid Layer; Smear Layer; Etch and Rinse; Self Etch Adhesive

### Introduction

Restorative dentistry cannot be accomplished without the use of a dental adhesive system. Dental adhesives not only provide bonding in cases of resin restoration but also provide retention in a wide range of indirect restoration like inlay, onlay, veneers, and ceramic

crowns. The adhesive system in dentistry is used in various procedures like during application of pit and fissure sealants, obturation using resin-based obturation materials, treatment of dental hypersensitivity, and adhesion of orthodontic brackets. Advances in dental adhesive systems help in the advancement of modern restorative dentistry [1]. Adhesive Dentistry helps in the conservation of tooth structure, restoration using a tooth-colored resin material, and ceramic crown uses the concept of dental adhesion and reduces the amount of tooth structure compromised in the conventional cavity and tooth preparation [2].

**History of dental adhesives**

In 1955 Buonocore first proposed the use of adhesion technology in dentistry by acid etching of the enamel leading to adhesion on the tooth surface to bond resins. Another material invented was Sevritron Cavity Seal, which was a mixture of glycerophosphoric acid and dimethacrylate in 1949 by Oskar Hagger in 1952, Kramer and McLean established that this material could be used for chemical bonding to the tooth structure [3]. The earliest commercially available invention was pit and fissure sealant in the year 1960, which utilized adhesive technology. Buonocore gave the theory of the formation of resin tags by an etchant for micromechanical locking, which provided retention was the main action of bonding. By late 1960 Buonocore established that bonding could also be done to dentin. After that, dental adhesives that provided more strength and bonding to both enamel and dentin with a wider bonding interface have been developed [4]. Etch and rinse adhesives became popular around the year 1980. In 1982, Nakabayashi suggested bonding by the infiltration of monomers into the tooth structure. The Late 90’s modernized the concept of Hybrid layer and single-step adhesives [5]. Table 1 diagrammatically represents the evolution of the dental adhesive system [6].

1955s Proposed Dental Adhesive Technology
1956s First Generation
The mid-1960s Proposed Binding of Dentin Commercially Available Pit and Fissure Sealant and Composite Resins Utilizing Bonding
The late 1960s Proposed Bonding of Dentin
The 1970s The Beginning of Both concept of Total Etch and Smear layer
Late 1970s Second Generation
Late 1980s Acceptability of Etch and Resin Adhesive
1980s Third Generation
1990s Acceptance of the “Hybrid Layer” Concept Availability of Multi-Step, Single Step Adhesives, and The Concept of Wet Bonding.
Early 1990s Fourth Generation
Mid 1990s Fifth Generation
The late 1990s the Concept of Smear Layer Modification: Self etch Adhesives Developed from the First and Second Generation.
The late 1990s and Early 2000s Sixth Generation
Late 2002s and Early 2005s Seventh Generation
The 2010s Eight Generation
2011s Universal Adhesives

**Table 1:** Evolution of the dental adhesive system [6].

### Classification of dental adhesive system

The classification of dental adhesives can be done based on various categories [6]:

1. Smear Layer
  - I. Modification of smear layer
  - II. Dissolving the smear layer
  - III. Removal of smear layer
2. No of steps:
  - I. Etch and rinse
    - i. 3 step system
    - ii. 2 step system
  - II. Self etch
    - i. 2 step system
    - ii. 1 step system [7].
3. Based on generation
  - I. **1<sup>st</sup> generation:** 2 steps involved, bond strength around 1 - 3 MPa. Based on Bunoucore's technology of NPG-GMA and later, Bowen introduced the use of NPG-GMA as a primer to reduce the reduction in strength on immersion in water [6].
  - II. **2<sup>nd</sup> generation:** 2 steps involved, bond strength around 4 - 6 MPa. Polymerised phosphates were added to Bis GMA, and they bonded with the calcium in the tooth structure. This failed to bond with the smear layer and hence is no longer used [8].
  - III. **3<sup>rd</sup> generation:** 3 steps are involved, and bond strength is 12 - 15 MPa. The dentin was acidly etched in this generation hence removing the smear layer or modifying it to increase the bonding. Tubules of the dentin open after etching, and a primer was applied once the etchant was removed [8].
  - IV. **4<sup>th</sup> generation:** 3 steps involved, bond strength around 25 MPa. 4<sup>th</sup> generation involved the complete removal of the smear layer and is still considered the gold standard. The etchant, primer and the bonding agent are all supplied in separate bottles and applied one after the other. The highlights of the 4<sup>th</sup> generation were "wet bonding" to avoid the collapse of collagen, thus forming a hybrid layer and reduction in marginal leakage. The only drawback of this generation was the use of multiple bottles, thus complicating the procedure [9].
  - V. **5<sup>th</sup> generation:** 2 steps are involved; bond strength is around 25 MPa. The main modification in this generation was the supplication of the process by reducing the no of steps. This involved combining the primer and adhesive into a single bottle, etching of tooth surface using 35 - 37% phosphoric acid for 15 - 20 seconds followed by the application of

adhesive and primer. The main disadvantage of this system was high susceptibility towards water degradation because of polymerized primer, which is hydrophilic in nature [10].

- VI. 6<sup>th</sup> generation:** 1 step involved, bond strength 20 - 40 MPa. This generation introduced the concept of a self-etching primer. The procedure is comprised of the application of the acidic primer followed by adhesive or combination of the two mixed just before followed by application on the tooth surface. The main advantage of this generation was independence from the state of hydration of the dentin. Although the bonding to dentin was better in the 6th generation, bonding to dentin was weaker [11].
- VII. 7<sup>th</sup> generation:** 1 step is involved; bond strength is 20 - 40 MPa. All the ingredients were put in a single bottle, which eliminated the complexity of multiple steps and hence reduced failure due to manual error. The main disadvantage was hydrolysis of the ingredients leading to degradation of the bond hence reducing the bond strength [12]. Another disadvantage was that the acidic content of the ingredients makes them more hydrophilic hence causing voids after application [11].
- VIII. 8<sup>th</sup> generation:** 1 step is involved; bond strength is 30 - 50 MPa. Manufactured by voco America, the Futurabond was introduced in the year 2010 and classified as the 8<sup>th</sup> generation. The main concept was the introduction of nanofiller, which increased the penetration of the monomer and the thickness of the hybrid layer. The main advantage was increased bond strength, better stress distribution and increased shelf life [13].

Table 2 shows examples of various generations available in the market and used in clinics [6].

Generation	Available Brand
4 <sup>th</sup> generation	<ol style="list-style-type: none"> <li>1. All bond 2 (Bisco Schaumburg, IL, USA)</li> <li>2. Adper Scotchbond Multipurpose (3M ESPE, USA)</li> <li>3. Gluma Solid Bond (3M ESPE, Germany)</li> <li>4. Optibond Dual cure (Kerr, Orange, USA)</li> <li>5. Amalgabond (Kerr, Ultradent)</li> <li>6. Bond It (Dentsply, Caulk)</li> </ol>
5 <sup>th</sup> generation	<ol style="list-style-type: none"> <li>7. Solobond M (Voco, Germany)</li> <li>8. Excite DSC (Ivoclar Vivadent, Lichtenstein)</li> <li>9. Optibond Soloplus (Kerr, USA)</li> <li>10. Prime and Bond 2.0 (Konstanz, Germany)</li> <li>11. Prime and Bond NT (Konstanz, Germany)</li> <li>12. Adper Singlebond Plus (3M ESPE, Germany)</li> <li>13. Scotchbond 1 (Kuraray, Japan)</li> <li>14. Clearfil SE (Kuraray, Japan)</li> </ol>

6 <sup>th</sup> generation	<p>15. Clearfil Linear bond 2V (Kuraray, Japan)</p> <p>16. All Bond SE (Bisco, USA)</p> <p>17. iBond Gluma inside (Hanau, Germany)</p>
7 <sup>th</sup> and 8 <sup>th</sup> generation	<p>18. Xeno IV (Dentsply, USA)</p> <p>19. Clearfil DC Bond (Kuraray, Japan)</p> <p>20. Adper Easy one (3M ESPE, Germany)</p> <p>21. OptiBond All in one (Kerr, USA)</p> <p>22. Futurabond DC (Voco, Germany)</p>

**Table 2:** Shows examples of various generations available in the market and used in clinics [6].

**Mechanism of adhesion to dental tissue**

**Etch and rinse:** Considered as the gold standard of adhesion technology. It can either be three-step or two-step, which contains the application of etchant, which is phosphoric acid, then primer, then the adhesive resin, and two steps in which the second and third step is combined but etch and rinse is still followed. The increased bonding strength of this system is mainly attributed to the usage of phosphoric acid in the concentration of 34 - 37%, which removes the smear layer. The hybrid layer is formed, which is an interdiffusion layer [14].

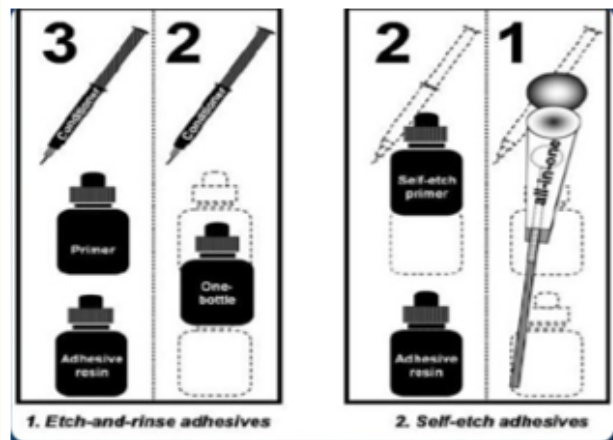
The acid etching of enamel produces micro and macro tags, which facilitates easy penetration of resin by capillary action. The resin infiltrates the tags and, after polymerization, form a very strong bond with enamel. The adhesion in dentin is more challenging compared to enamel because of the structural composition of dentin. After the etching of the dentin, the collagen fibrils are exposed, which are devoid of hydroxyapatite. This is overcome by the application of hydrating primers like HEMA (2-Hydroxy ethyl meth-acrylate) that are mixed in a solvent, which is water or ethanol based. Since HEMA is hydrophilic in nature, it makes the collagen re-expand, and the solvent helps to displace the water part of dentin. Followed by this is the bonding step in which a resin is applied that does not contain any solvent, which leads to the penetration of monomer deep into the collagen fibrils as well as the dentinal tubules. Once infiltration is complete, polymerization of the resin takes place, which forms a layer called the hybrid layer and together with the polymerized resin in the dentinal tubules, give retention to composite restoration [15].

The two-step modification of this etch and rinse process involves the combination of primer and the bonding resin into a single solution. This solution is not able to infiltrate the collagen completely and hence leading to a suboptimal hybridization. The adhesive is hydrophilic in nature, which leads to hydrolytic degeneration. The main drawback of etching and rinse technique is failure due to human error like over-drying of the dentin, which leads to the collapse of collagen fibers and does not let an optimum hybrid layer to form. Apart from over-drying, over wetting of the dentin is also a problem as it leads to the formation of voids or blisters in the resin-dentine interface. Over-wetting also prevents the complete polymerization of the resin, which causes a decreased quality of the hybrid layer, causing early degradation. To avoid the chances of over wetting and over-drying, the mechanical procedure should be done with the utmost caution, which includes drying of the enamel up to a point where frosty white appearance is seen, and the dentin becomes dull. Another disadvantage of this system is the inability to reduce nanoleakage, which leads to reduced durability of the bond. To overcome all the drawbacks, self-etching adhesives were formed [16].

**Self-etch adhesives:** The main motivation of developing the self etch adhesive was to reduce the sensitivity of the etch and rinse technique due to the chances of mechanical error due to an increased number of clinical steps [17].

The self-etch adhesives can be classified based on [17]:

1. Acidity
  - a. Strong (pH < 1)
  - b. Intermediate (pH ~1.5)
  - c. Mild (pH > 2)
2. No of steps
  - a. Two-step procedure - Self etch primers (SEP)
  - b. One step procedure - Self etch adhesives (SEA) (Figure 1).



**Figure 1:** Classification adhesive system based on number of steps [7].

The mild self-etch adhesive leaves the hydroxyapatite around collagen fibrils free for chemical interaction as it causes demineralization of only the top layer of the dentin. In some cases, the smear plus is not removed, leading to the formation of a shallow hybrid layer; on the other hand, the strong self-etch adhesive is comparable to etch and rinse adhesive. The mild adhesive causes less flow of the dentinal fluid because of the presence of smear plugs, thereby leading to less postoperative pain. The main component of self etch adhesive is HEMA, which causes increased miscibility of hydrophobic and hydrophilic layer, increasing the wetting ability of the dentin. The smear layer that is formed after the tooth preparation is also altered by the self etch adhesives, thus creating a hybrid layer that is 0.5 - 1.5 mm thick. A chemical bond is seen with the tooth structure in this system. Additionally, due to the presence of residual smear layer, there is less flow of dentinal fluid hence reducing the hypersensitivity [18].

In the two-step self-etching system, two components are used, namely a primer and acid combined in one bottle followed by resin. The SEP contains an acidic solution with monomer, which etches and infiltrates the dental tissue at one followed by photopolymerization of the resin [19]. The two-step self-etch adhesive system is explained by the AD effect (Adhesion-Decalcification) which says that all the acid combines with the calcium of the tooth and form ionic bonds, but later due to the instability of the calcium phosphate/carboxylate

compound it is finally debonded leading to the removal of calcium from the enamel/dentin surface giving an etched pattern, which leads to the formation of a suitable hybrid layer [20]. When the self-etching primer and bonding agent are combined, then a single step self-etch adhesive system is formed. According to the number of components, the SEA is divided into two categories i. Single component ii. Two-component. The two-component SEA has a longer shelf life, but the mixing of the components just before the application is required. The single-component combines all the ingredients into one bottle; hence is the true “single bottle” or “all in one” adhesive. This adhesive system is classified as the 7th generation adhesives and is the most convenient and ideal way of adhesive application. The main disadvantage was hydrolysis of the ingredients leading to degradation of the bond hence reducing the bond strength. Another disadvantage was that the acidic content of the ingredients makes them more hydrophilic hence causing voids after application [12].

### Universal adhesive system

In 2011, the universal adhesive was introduced. These adhesives are also called Multi-mode or multi-purpose as they can be used both as self etch or etch and rinse or both on dentin and enamel, respectively (Selective Enamel Etching) [21]. Etching of the enamel with phosphoric acid is advised in both the case. Bonding to dentin is achievable with both etch and rinse, and self etch adhesives, but enamel bonding is better when the etch and rinse approach is used [22]. Self etch adhesive systems are not able to etch enamel at the same level as phosphoric acid, and hence marginal discoloration can be seen cervically. Thus the universal system of adhesive has been developed, which involves pre etching of the enamel before selective or total-etch approach, thus increasing the strength [23]. The composition of the adhesive is also of utmost importance as the carboxylate and phosphate monomer combine to the calcium in hydroxyapatite. Methacryloyloxydecyl Dihydrogen phosphate (MDP) is the main component of the new universal adhesive, which leads to the formation of stable Calcium MDP compounds, which are arranged in Nanolayers [24,25]. Some universal adhesives may also contain silane thereby eliminating the silanization process when bonding ceramics or glass. The simplified single step bonding procedures have shown lower bond strength, and hence the multi approachability helps clinicians decide between total etching and selective etching, thus giving a much wider application than that of the 7<sup>th</sup> generation [26].

### Conclusion

During the current rage of conservative dentistry, dental adhesives have a huge role in the preservation of tooth structure. Apart from that, this leads to restoration using resin bonded tooth-colored materials, thereby enhancing the esthetics of dental restorative procedures. This review is an accumulation of all the classifications and mechanisms of the dental adhesive system available in the present era.

The adhesive system has been classified in etch and rinse, and self etch adhesives and also according to the advent and generations of the adhesives. With time clinicians are trying to introduce bonding agents with the highest bond durability and least degradation. Every generation has overcome the drawback of the previous generation and simplified the clinical procedure of the application of the bonding agent. The modern adhesive systems have overcome issues of postoperative sensitivity, microleakage and flow of the resin. The chemical bonding to tooth structure like the usage of MDP is also a crucial development in the dental adhesive system.

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