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Review Article

Bonding Performance of Universal Adhesive in Different Etching Modes: A Review

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ABSTRACT

The field of dentin bonding agents has evolved significantly over the past four decades as a result of the challenging pledge to use resin monomers to achieve better adhesion to dentin. A new class of adhesives known as Universal Adhesives (UAs) has been developed in response to the growing demand for user-friendly and simplified adhesive solutions. The word "universal" refers to the adhesives' ability to be used with a wide range of direct and indirect restorative materials, according to the producers, and can be applied with any adhesion approach that is with both the etch-and-rinse and the self-etch techniques. This review article highlights the chemical composition, function and mechanism of universal adhesion. It also reviews the potential of adhesion in both etch and rinse and self-etch mode for both enamel and dentin substrate and their clinical significance.

KEYWORDS: Universal bonding, Etching mode, Self-adhesive, Etch-and-rinse, Self-etch

INTRODUCTION

For a very long period, amalgam was the preferred material for restoring teeth that had been decayed, which resulted in the large macro-retentive cavities. However the concept has evolved from the GV Black proposed restorative principle of "Extension for Prevention" into "Prevention of Extension," also referred to as "Minimal Intervention Dentistry." The goal of minimally invasive procedures is to limit the amount of sound tooth structure that needs to be removed during cavity preparation. Resin composites have steadily shown to be the most recommended restorative material, that fits into this concept. However, this process always necessitates an intermediate bonding agent that enters the dentin and/or enamel and mainly creates what is known as micromechanical bonding.

In the past 40 years, dental adhesives have undergone significant chemical and component changes as a result of the challenging pledge to use resin monomers to achieve better adhesion to dentin. The efficiency provided by the simplified bonding processes has made self-etch adhesive systems highly popular in recent years. Additionally, it is believed that chemical bonding and lessened dentin demineralization contribute to the incidence of post-operative sensitivity appearing to be reduced in comparison to etch-and-rinse systems.

A new variety of single-step self-etch adhesive has only recently been released. Being able to be utilized with both the etch-and-rinse and the self-etch techniques, this kind of self-etch adhesive is referred to as "universal" or "multi-mode". In order to increase the longevity of the enamel bond, universal methods let applying the adhesive after pre-etching with phosphoric acid in either the total-etch or selective-etch procedures. It also offers an easier technique for using the self-etch process on dentin.

Universal Adhesive:

The restorative and preventive dentistry have begun to evolve as a result of the invention and widespread usage of adhesive materials. With these adhesive materials, it is no longer required to prepare the cavity to offer mechanical retention through features like dovetails, grooves, undercuts, and sharp internal angles in order to retain the restorative material. As a result, approach towards cavity preparation are undergoing change.

(1). Therefore, these methods prevent the loss of significant amounts of healthy tooth substance that would have been lost otherwise by the dental bur. It may be possible to prevent microleakage, a serious dental issue that is undoubtedly to blame for a large number of secondary caries. For the success of aesthetic materials restorative in contemporary dentistry, these adhesives are therefore essential. Dental adhesives are solutions of resin monomers that enable the interaction of resin with dental substrates.

(2). Monomers with both hydrophilic and hydrophobic groups make these adhesive systems. The latter enable interaction and co-polymerization with the restorative material, while the former improve wettability to the tooth hard tissues. Additionally, curing initiators, inhibitors, or stabilizers, solvents, and, in rare situations, inorganic fillers are included in the chemical composition of adhesives.

(3). However, it is important to take into account dental anatomy. Understanding the composition and structure of the two major tissues, enamel and dentine, in particular, is necessary to comprehend how they affect adhesive bonding. Whereas the dental hard tissues latter enable interaction and co-polymerization with the restorative material.

Major Component Of Universal Adhesive :10-MDP

Fig 1 chemical structure of 10-MDP

Function:

1. Methacrylate functional group for polymerization
2. Phosphoric acid ester functional group for ionic bonding with Ca of HAp (adhesion route)
3. Spacer with adequate length:

A. Efficient separation of both functional end groups

B. Provides hydrophobicity

4. Phosphoric acid ester functional group for etching: Enables micro-mechanical interlocking and Nano layering

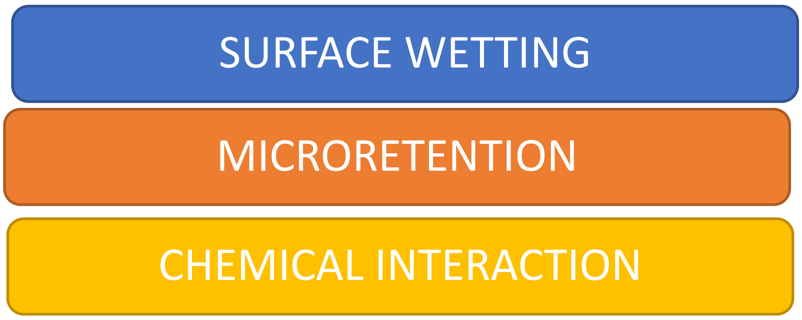
Acidic functional monomers are the primary functional components of (ultra)mild self-etch adhesives, among that the functional monomer 10-MDP has received the most attention for its propensity to form chemical bonds. Such Functional monomers enhance the bonding potential of the micro-retention created by the minimal surface decalcification and etching effect of the acidic functional monomer. This enhancement occurs through the interaction of their phosphate groups with the calcium atoms of hydroxyapatite (HAp).

Designing a modified Adhesion Route was necessary due to the specific chemical interaction of 10-MDP with HAp. Among many acidic functional monomers, 10-MDP chemically (ionically) binds to the Ca in HAp but also etches the HAp-based substrate, liberating significant amounts of Ca in the process. A stable 10-MDP-Ca salt is formed in response to such Ca release, which leads 10-MDP to self-assemble into approximately 4-nm nanolayers.

Fukegawa et al. In 2006 were the first to chemically validate this structure. It was discovered that CaRPO4 made up the hydrolytically stable 10-MDP-Ca salts, indicating that the two hydroxyl (OH) groups of the phosphate group of 10-MDP interacted ionically with Ca. This solid structure is anticipated to help the hybrid and adhesive layer's hybrid and adhesive layer's 10-MDP-Ca salts form durable nanolayers, extending the clinical lifespan of the adhesively bonded restoration.

Mechanisms Of Adhesion:

The main adhesive mechanisms of any dental material designed to bond to tooth tissue include



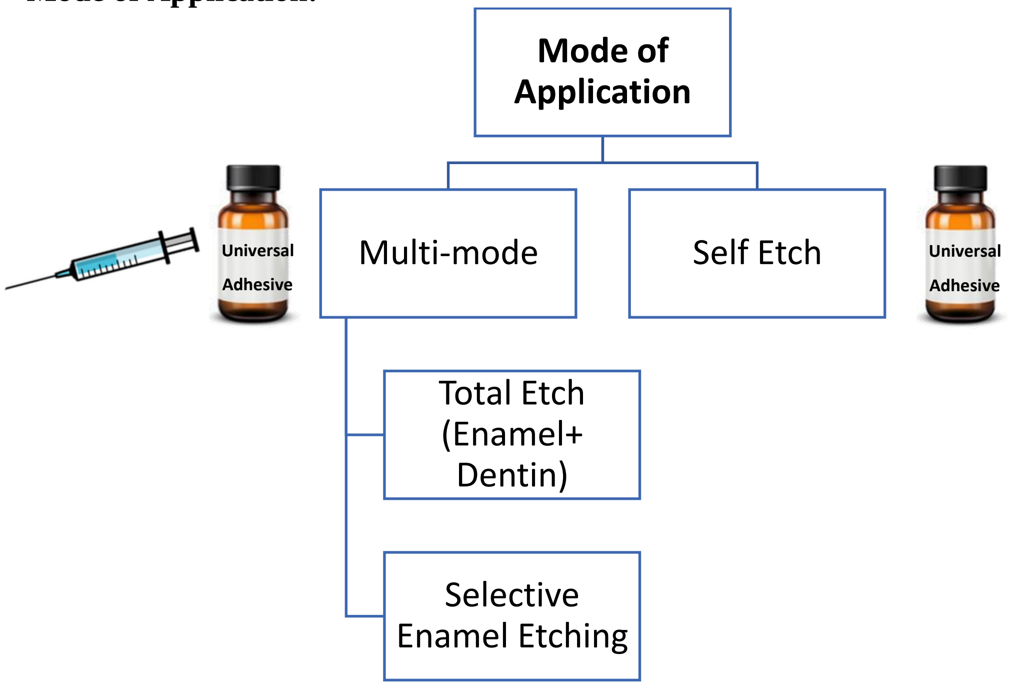
Ensuring sufficient surface wetting is crucial to establishing effective contact between the adhesive material and the adherend or substrate. The surface tension of a liquid must be lower than the free surface energy of the substrate in order for it to spread evenly across a solid surface. Contact angle measurements, which should ideally be close to zero, are frequently used to predict surface wetting behaviour.

The natural viscosity of non-liquid materials, like self-adhesive luting and restorative composites, hinders their ability to spread consistently over surfaces for extended periods. Various factors contribute to this limitation, that includes:

1. Surface roughness
2. Differences in substrate surface energy, ranging from high (e.g., etched enamel) to low (e.g., dentin covered with smear layer)
3. Factors that enhance bonding, like capillary forces (e.g., bonding to etched enamel)
4. Surface hydrophilicity/ hydrophobicity
5. Interfacial gaps (containing air or moisture) that compromise bond strength

Materials that can form bonds should start out being hydrophilic (having a low water contact angle) to effectively wet moist dentin. However, it's preferable for them to change to a hydrophobic state (having a high water contact angle) upon polymerization. This transformation helps prevent water absorption and the degradation of the bond due to hydrolysis. This is because dentin is an intrinsically wet tissue (liquid-filled tubules), making it difficult to bond. The equilibrium between hydrophilicity before curing and hydrophobicity after polymerization should therefore be achieved by adhesives. Given the extraordinarily high permeability of dentin, which has multiple dentin tubules connecting it directly to the pulp in addition to its highly microporous inter-tubular dentin structure, hermetically sealing adhesive-dentin contacts is essentially impossible. But debris is spread and compacted throughout enamel and dentin, interfering directly with surface wetting. (Mine et al, 2014)

Mode of Application:



Adhesion:

The techniques for bonding adhesives to enamel and dentin primarily involve surface demineralization, infiltration of resin monomers, and subsequent polymerization. This process creates micro-mechanical interlocks within the generated porosities. This process, known as "hybridization," creates a hybrid layer on the dentin that contains collagen fibers that have been penetrated with resin. The collagen fibrils are made evident by phosphoric acid etching of the dentin (30–40%), which induces superficial demineralization and aids in the removal of the smear layer. The smear layer serves as a physical barrier that prevents monomers from penetrating the surface. In order to create a hybrid layer that is integrated with the dentin, more monomers must be impregnated into the surface as a result of the phosphoric acid etching. However, self-etching adhesives do not need to etch dental substrates with phosphoric acid since they contain acid resin monomers that concurrently "condition" and "prime" the substrates. These adhesives do not eliminate the calcium phosphates; they merely dissolve the smear layer.

Commercially Available Universal Adhesives :

Name of the Material	Scotchbond Universal (3M)	Clearfil Universal (Kuraray)	Futurabond U (VOCO)	All Bond Universal (Bisco)	Premio Bond (GC)	Adhese Universal (Ivoclar)
Components	Dimethacrylate resins HEMA, Vitrebond™ Copolymer Filler Ethanol Water Initiators	Bis-GMA HEMA Ethanol 10-MDP hydrophilic aliphatic dimethacrylate colloidal silica dl-camphorquinone silane coupling agent accelerators initiators water	Bisphenol A diglycidylmethacrylate 2-hydroxyethyl methacrylate1,6-hexanediylbismethacrylate acidic adhesive monomer urethanedimethacrylate catalyst	Bis-GMA ethanol 10-MDP HEMA	10-MDP 4-MET MTDP methacrylic acid ester silica acetone water photo-initiators	2-hydroxyethyl methacrylate bisphenol A diglycidyl ether dimethacrylate ethanol 1,10-decandiol dimethacrylate methacrylated phosphoric acid ester campherquinone 2-dimethylaminoethyl methacrylate

Adhesion To Enamel:

Self Etch Strategy

Lower aggressiveness compared to phosphoric acid reduces their potential to fully demineralize enamel thereby resulting in inadequate retentive microporosities

Self etch produces significantly lower enamel micro-shear and micro tensile bond strength (µtbs) values. Rosa *et al. 2015*

Etch and Rinse

Etch and Rinse (ER) showed improved enamel bond strength values as compared to self etch(SE) technique. Diniz *et al, 2016*

Significantly better long-term bond characteristics. Takamizawa *et al, 2015*

Adhesion to Dentin:

Statistically similar average dentin micro tensile bond strength values of about 37 Mpa (Etch and Rinse) versus 35 mpa (Single Etch) strategies. Elkaffas *et al. 2018*

Testing dentin bond durability concluded that the self etch strategy resulted in more stable long-term bond characteristics, due to stable chemical bonding produced by 10-MDP. Sezinando *et al, 2019*

Stages of adhesive interface fail

The complete understanding of the degradation process of the hybrid layer remains unclear. However, the biodegradation of the adhesive interface follows a series of steps.

First stage

When dentin is acid etched, the process of removing the smear layer and exposing the underlying collagen network to facilitate the creation of the succeeding hybrid layer. The exposed collagen fibers are more vulnerable to potential degradation once the minerals are reduced.

Second stage

Resins that infiltrated into the dentin matrix are leached out and replaced by water, leaving gaps in the hybrid layer that are the size of nanometres.

Third stage

During this phase, the exposed collagen fibrils undergo enzymatic breakdown. Demineralized dentin triggers proteolytic enzymes (MMPs) responsible for degrading the exposed collagen fibrils during bonding procedures using both etch-and-rinse and self-etch systems.

Methods to Improve Bond Strength to Enamel:

- Prolonged application of the adhesive is a practical alternative to enamel etching. Cardenas *et al, 2016*
- Double application may be effective in enhancing enamel bond strengths, due to the increased thickness and improved mechanical properties of the adhesive layer. Fujiwara *et al, 2016*
- Application of additional hydrophobic resin coating. Reis *et al, 2014*

The mechanism of bonding to enamel etched with phosphoric acid is based on the micro-mechanical interlocking of adhesives into etch pits through selective demineralization of prismatic and aprismatic dental substrates. Despite manufacturers' efforts to improve the enamel bond strength the use of prior acid etching increases the enamel bond strength, and the etch-and-rinse strategy can be suggested for use to improve the adhesion to enamel.

In this context, self-etch and universal adhesives have a less acidic composition compared with phosphoric acid, thus reducing their potential to demineralize the full mineral phase of enamel and, consequently, to create appropriate micro-retentive porosities.

Clinical studies pointed out that enamel pre-etching resulted in a more durable marginal integrity of restorations bonded with self-etch adhesives

Methods to Improve Bond Strength to Dentin:

- SE strategy: applying additional hydrophobic resin coat, due to improvement in the degree of monomer conversion at the resin–dentin interfaces. Sezinando *et al, 2015*
- Active application (scrubbing) of the adhesive on the dentin surface irrespective of the adhesion strategy. Moritake *et al, 2018*
- Application of matrix metalloproteinases (MMPs) inhibitors such as Chlorhexidine, Benzalkonium chloride, polymerizable benzalkonium methacrylate, and ethylenediaminetetraacetic acid (EDTA). Sabatini *et al 2015*

Advantages of Universal adhesive:

- Combining primer and adhesive resin, UNIVERSAL ADHESIVES facilitate quick clinical bonding procedures, purportedly with reduced technique sensitivity.
- The term "UNIVERSAL" refers to their application possibilities, which enable them to be used either following an Etch and Rinse or self etch bonding mode, while offering application flexibility with bonding potential to glass-rich (via silane) and glass-poor zirconia (via 10-MDP) ceramics for indirect tooth-restoration indications.
- Bonding technique mainly utilizes micromechanical interlocking that is based on diffusion
- In the universal self-etch bonding approach, the inclusion of monomers containing an acidic functional group (such as phosphate or carboxylate) is crucial, as it is believed to simultaneously etch (demineralize) and penetrate dentin up to a depth of 1 μm.
- On enamel, the self etch bonding mode often works worse than the Etch and Rinse bonding mode, in which the enamel is still subject to selective phosphoric acid etching (Etch and Rinse). Nevertheless, self etch bonding has the possibility for chemical bonding, which is an additional advantage for achieving strong connection.
- 10-MDP (10-methacryloyloxydecyl dihydrogen phosphate) has several beneficial bonding properties: it etches dentin, releasing calcium; it ionically binds to calcium in hydroxyapatite (HAp); and it self-assembles into stable nanolayered calcium salts that disperse throughout the adhesive interface in three dimensions. Most dental manufacturers created 10-MDP-based Universal Adhesives because of 10-MDP's advantageous bonding characteristics.

Many of the commercially available adhesives that are now on the market are clinically effective in terms of initial performance (restoration retention, marginal sealing), though there is some product dependence.

Disadvantages of Universal Adhesives:

- The adhesive layer, often less than 10 μm thick, can face polymerization challenges due to oxygen inhibition. Inadequate polymerization may lead to water absorption from the underlying dentin through osmosis, potentially compromising the adhesive bond.

- Thin adhesive layer reduces the adhesive layer's capacity to withstand stress (polymerization shrinkage) placed on the adhesive interface.
- Many Universal Adhesives contain the mono-functional monomer HEMA. However, HEMA does not polymerize effectively, leading to a weak integration into the polymer network.
- The incorporation of silane, which many Universal Adhesives contain to chemically connect to ceramics that are glass-rich and eliminate the need for a separate ceramic (silane) primer, is the cause of the potentially degraded bonding performance of Universal Adhesives.

• Although the functional monomer 10-MDP forms an ionic bond with hydroxyapatite (HAp), creating a stable nano-layered monomer-calcium salt structure, the esters of 10-MDP linking the hydrophobic spacer to the methacrylate and phosphate functional groups at both ends of the monomer are prone to hydrolytic degradation.

Universal Adhesives offer the flexibility of application in full 2-Etch and Rinse, full 1-SE (Self-Etch), or a combined 2-step selective enamel Etch and Rinse phase followed by a 1-SE bonding mode. Many of these adhesives incorporate 10-MDP, which is considered one of the most effective functional monomers available today. Despite its widespread use, the exact role of 10-MDP in Universal Adhesives during the Etch and Rinse mode, which primarily relies on a diffusion-based micromechanical bonding mechanism, remains somewhat unclear. Some studies suggest that 10-MDP may interact chemically with collagen, but further research is needed to confirm the significance of these interactions for the long-term durability of the adhesive interface. It's worth noting that while most Universal Adhesives contain 10-MDP, variations in bonding performance may exist due to differences in the concentration and quality (purity) of 10-MDP, both of which have been shown to impact bonding effectiveness.

Clinical Significance:

A. Aim to preserve as much enamel as possible on cavity margins.
B. Remove all infected dentin.
C. Remove caries-affected dentin from surrounding walls, keeping it at pulpal and axial walls.
D. Maintain the appropriate dentin humidity based on the bonding agent used.
E. Use selective acid etching for self-etch agents when cavity margins are on enamel.
F. Clean cavities with an anionic detergent before continuing with the restorative protocol.
G. Ensure your curing unit emits the correct wavelength for the photoinitiators of the bonding systems; adhere to the manufacturer's instructions.
H. When opting for self-etching strategies, give preference to those promoting chemical adhesion to the dental substrate, especially those based on 10-MDP
I. An extra coating of hydrophobic resin should be applied over dentin treated with any of the currently available simplified bonding agent

CONCLUSION

Within the limitation of laboratory studies and clinical randomized evaluations, it suggests that the application of universal adhesives using some alternative etching techniques may be beneficial for improving the bonding performance to dentin.

The use of multi-mode adhesives enhances bond strength when acid etching is applied only to enamel; however, this improvement is not observed for dentin with mild universal adhesives. Therefore, selective enamel etching may be the most effective approach for maximizing bond strength with mild universal adhesives. On the other hand, the adhesive properties of universal adhesives to dentin depend on the material used, regardless of the adhesion strategy.

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