



Modern Adhesive Dentistry: A review of literatures

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ABSTRACT

Adhesion (bonding) comprise a complex set of physical, chemical, and mechanical mechanisms that allow the attachment and binding of one substance to another. An adhesive is a material, frequently a viscous fluid, that joins two substrates together by solidifying and transferring a load from one surface to the other. For good adhesion, close contact must exist between the adhesive and the substrate (enamel or dentin). For better wetting and infiltration to the dental substrate, the adhesive's surface tension should be lower than the surface free energy of the substrate.

Keywords: Adhesive systems, Enamel, Dentin substrates.

INTRODUCTION

The dental adhesive system performs mainly three important functions: (1) they resist the separation of the adherend substrate (i.e., dentin, enamel, composite, ceramic, metal restorations) from the restorative or cementing material; (2) they distributes the load across the bonded interfaces; and (3) they seal the adhesive interface by adhesive bonding between the dental substrate and the restorative materials enhancing their resistance to bacterial microleakage, reduce the risk of postoperative sensitivity, prevent marginal staining and secondary caries development (Bedran-Russo et al., 2017).

The first trials of Buonocore's to achieve bonding to enamel in 1955 and to dentin in 1956 had a great revolutionary effect in adhesive dentistry. Because of the enamel nature and composition, enamel bonding has been predictable, while good bonding to dentin remains more challenging and questionable. This is due to the nature of dentin, its wettability, and its heterogeneous composition (Pashley et al., 2017) .

All dental adhesive systems are based on polymeric resinous materials. These materials have a variety of chemical characteristics, ranging from very hydrophilic to very hydrophobic. The ability of dental adhesive systems to bond to tooth structures is currently recognized to depend on two main factors (Bedran-Russo et al., 2017) :

- 1 .Substrate demineralization, which partially removes the mineral-phase and increases receptivity of the tooth .
2. Subsequent passive infiltration of the adhesive monomer into the demineralized layer.

CLASSIFICATION OF THE CONTEMPORARY DENTAL ADHESIVE SYSTEMS

Dental adhesives are often commercially categorized into generations reflecting the technique of handling or advances in the materials formulations rather than new concepts or mechanisms in adhesion (Anusavice *et al.*, 2013). By taking a close look into the chemistry of contemporary dental adhesives and their mechanism of adhesion to dentin, two major concepts in adhesion can be concluded (Van Meerbeek *et al.*, 2020):

1. The first one relies on the complete removal of smear layer (i.e., the layer of organic and inorganic debris left after cavity preparation) and demineralized superficial enamel and dentin.
2. The second concept depends on superficial, partial demineralization, and incorporation the smear layer into the adhesive-interface.

Both concepts promote adhesion through micromechanical retention to the underlying dental substrates. However, an additional chemical bond to the dental substrates is present, particularly in the latter concept (Van Meerbeek *et al.*, 2020).

Multiple or single steps are commercially available within the two major categories of systems, being referred to as etch & rinse and self-etch. Etch-and-rinse systems (also known as total-etch) require separate acid etching and rinsing steps followed by application of the primer and the adhesive in 2 separate or one combined step. Self-etch systems do not require a separate etching step; rather, an acidic primer is used to promote partial dissolution of the smear layer and infiltration of primer followed by application of the adhesive (2-step systems) or through a single formulation with an adhesive resin (all-in-one system) (Cardoso *et al.*, 2011; Bedran-Russo *et al.*, 2017).

Current dental adhesive systems have improved clinical procedures regarding both the evolution of their components, mechanism of action, and regarding the reduction of the application operative time. More recently, the term ‘universal’ has been used to define dental adhesive system that can be applied in different adhesion modes aimed to reduce the clinical complexity of the application procedures (see Figure 1-1) (Kaczor *et al.*, 2018).












Contemporary Dental Adhesive Systems					Characteristics			Longevity
System Mode	Delivery	Adhesion Steps			Acidity	Hydrophilicity	Bond Stability ^b	
		Etching	Primer	Adhesive				
Etch-and-rinse	3-step				+	+	++++	Stability Degree of Conversion Solvent Evaporation
	2-step				++	++	+++	
Self-etch	2-step				+++	++	++++	Acidity Hydrophilicity Degradation
	1-step				++++	+++	+	
Universal	1 or 2 steps ^a				+++	++	+(+) +	

Figure 1-1: Classification of contemporary dental adhesives systems and their various characteristics which affect the long-term stability of the adhesive interfaces. Symbol (+) indicates scale ranged from the lowest to highest (+++++) (Bedran-Russo *et al.*, 2017).

CHEMISTRY OF CONTEMPORARY DENTAL ADHESIVE SYSTEMS

Dental adhesives are mainly consisted of three major constituents: (1) etchant, (2) primer, and (3) the adhesive resin (**Hilton *et al.*, 2016; Dressano *et al.*, 2020**).

Dental bonding agents are designed to provide strong interfaces between the restorative composite fillings and the tooth structure that can withstand the mechanical forces and shrinkage stresses. Therefore, each constituent of a dental adhesive plays an important role in the adhesive procedure as following (**Van Meerbeek *et al.*, 2020**):

ETCHANT

The etchant is composed of acidic molecules that remove or alter the smear layer and demineralize the enamel and dentin to be prepared for bonding. Many etching solutions have been tested, including those containing phosphoric (10 %- 50 %), fluoridated-phosphoric, citric, maleic, pyruvic, oxalic, tannic, ethylenediamine-tetra acetic, and polyacrylic acids. However, phosphoric acid at concentration from 30% to 50%, typically 37%, is the preferred etching agent to produce consistent etching patterns without damaging the pulp. Generally, the etchant is supplied as an aqueous-gel of fumed-silica of cellulose-beads, to allow precise placement of the etchant over a specific area. Given the histologic characteristics differences between enamel and dentin, the etching considerations of those substrates can differ vastly (**Hilton *et al.*, 2016**):

ETCHING OF ENAMEL

Enamel etching can substantially enlarge the surface area available for adhesive and can almost doubles the free surface energy. Three morphologic patterns of etching to enamel have been described. Etching Type-I removes the cores of enamel prisms while leaving the periphery intact; etching Type-II removes the enamel prisms periphery while leaving the core relatively intact; and etching type-III takes a random approach characterized by a combination of types-I and types-II resulting in morphologically un-classified pattern. These etching patterns are determined by the enamel mineral content and morphologic characteristics (**Hilton *et al.*, 2016**).

Enamel etching creates micro-porosities within which resin-tag extensions of the adhesive monomers can micromechanically interlock. *Macrotags* form between enamel-prism peripheries, and *microtags* form in the prism's cores (**Swift *et al.*, 2018**).

ETCHING OF DENTIN

Total-etching technique revolutionized by **Fusayama's** to treat dentin was initially resisted by dentists, who feared that adverse reactions to the pulp would result from the use of 40%-phosphoric acid. Subsequent studies concluded that such reactions are mainly related to bacterial leakage, rather than the effect of acid etchant, which could be used useful on dentin more than 0.5 mm thick, to provide effective sealing to the etched dentin (**Breschi *et al.*, 2007; Van Meerbeek *et al.*, 2020**).

The use of phosphoric acid to etch dentin removes the smear layer, demineralizes the first 5-7 μm of dentinal substrate, and creates funnel-shaped dentinal tubules. The latter effect is related to the presence of higher contents of minerals in peritubular dentin than the intratubular dentin. Acid etching thus makes the dentin porous, allowing the infiltration and impregnation of the adhesive components (**Özcan *et al.*, 2012**).

Several studies have investigated the effects of different etching-times on bond strength to dentin. The determination of appropriate etching time should consider (1) the monomers ability to infiltrate the substrate in relation to dentin demineralization depth and (2) the

ability of collagen fibrils to maintain their integrity when exposed to phosphoric acid at a given length of time (**Zheng *et al.*, 2014**).

Clinicians should seek to demineralize dentin only to the desired extent of infiltration. Excessive dentin demineralization may produce a weak zone comprised of sub-optimally impregnated dentin at the base of the hybrid layer consisting of exposed collagen fibrils. Thus, etching should be limited to superficial dentin because the viscosity of primers and adhesive agents allows only a few micrometers of infiltration (**Özcan *et al.*, 2012; Hilton *et al.*, 2016**). Several studies have found that prolonged acid-conditioning times resulted in fracture within the demineralized dentin zone when specimens were stressed to failure (**Perdigao *et al.*, 2019**). The results of those studies indicate that dentin should be etched no more than 15 seconds (**Maravic *et al.*, 2017**).

PRIMER

Primers are adhesive promoting agents, contain amphipathic resin monomers dissolved in organic solvents (i.e. acetone, ethanol and/or water) (**Agee *et al.*, 2015**). Primers are consisting of mixture of resin monomers, such as hydroxyethyl methacrylate (HEMA), triethyleneglycol dimethacrylate (TEGDMA), bis-GMA, and urethane dimethacrylate (UDMA), which have a varying degree of hydrophilic and hydrophobic properties (amphipathic). Hydrophilic functionality facilitates monomers penetration into collagen matrix to form a hybridized collagen-resin layer, and hydrophobic functionality facilitates copolymerization to the resin matrix (**Shin *et al.*, 2009**).

HEMA is the most frequently used monomer in primers. Its low molecular weight and its hydrophilic nature not only enhances dentin wettability and penetration, but also potentiates re-expansion of the collagen fibrils network, improving bonding capacity of adhesive agents. Also, it enhances dispersion of hydrophobic monomers as it keeps them in adhesive solution, preventing phase separation of monomers (**Zheng *et al.*, 2014**).

Solvents are added to reduce the inherent viscosity of the co-monomers blends, allowing them to infiltrate the wet demineralized dentin matrix. Solvent type in primers has been found to affect the strength of bonding to dentin by enhancing the ability to re-expand a previously dried demineralized collagen matrix (**Spencer *et al.*, 2000**).

ADHESIVE RESIN

The adhesive systems consist of a blend of methacrylate-based adhesive monomers with either two cross-linking monomers or one functional monomer with polymerizable ends (Figure 1-2), organic solvents, a photo initiator system, and sometimes nano fillers. The primary purpose of adhesives is to fill the collagen interfibrillar space, creating a hybrid layer and resin tags to provide micromechanical retention upon polymerization. Also, the adhesive layers should prevent fluid leakage along the restorative material's margins (**Anusavice *et al.*, 2013; Perdigao *et al.*, 2019**).

The chemistry of dental adhesive resins must fulfill the requirements for adhesion to different kinds of the dental substrates (i.e. enamel, dentin, cementum). The functional hydrophilic resin monomers can facilitate resin diffusion into the demineralized/moist dentin, whereas the cross-linking hydrophobic resin monomers provide the mechanical strength, stability, and compatibility between the adhesive resin and the bulk restorative materials or resin cements (**Bedran-Russo *et al.*, 2017; Dressano *et al.*, 2020**).

Thus, resin monomers with two or more polymerizable ends are essential to establish a highly cross-linked polymer network to provide the strength and stability of the adhesive layer. Some examples of cross-linking monomers with a hydrophobic nature are bisphenol A-glycidyl methacrylate, triethylene glycol dimethacrylate, urethane dimethacrylate, and

ethoxylated bisphenol-A dimethacrylate. The difference in molecular weight among the resin monomers is important, because low-molecular-weight monomers dissolve the high-molecular-weight monomers, enhancing the wettability of the resin monomer blends (Shin *et al.*, 2009; Bedran-Russo *et al.*, 2017).

Functional monomers usually contain functional groups (e.g. hydroxyl groups) and a single polymerizable group to form the polymer chains (Malacarne *et al.*, 2006). In self-etch adhesive agents, the functional groups of resin monomers are usually acidic in nature for etching the enamel and dentin surfaces. Examples of acidic functional resin monomers are 4-methacryloyloxyethyl trimellitate anhydride (4-META), 10-methacryloyloxydecyl dihydrogenphosphate (10-MDP), and 2-(methacryloyloxyethyl) phenyl hydrogenphosphate (Phenyl-P. Functional groups with self-etching ability are either carboxyl or phosphate, and they can also establish ionic chemical bonds with calcium in the hydroxyapatite) (Van Landuyt *et al.*, 2007).

Overall, 10-MDP monomer is the most popular and highly stable acidic monomer. Its stability is related to the long carbonyl chain (spacer) between the functional group and the polymerizable end (Figure 1-2). Additionally, the phosphate functional group can form strong ionic-bonds with hydroxyapatite, owing to the low solubility of the resulting calcium-salts (Dressano *et al.*, 2020).

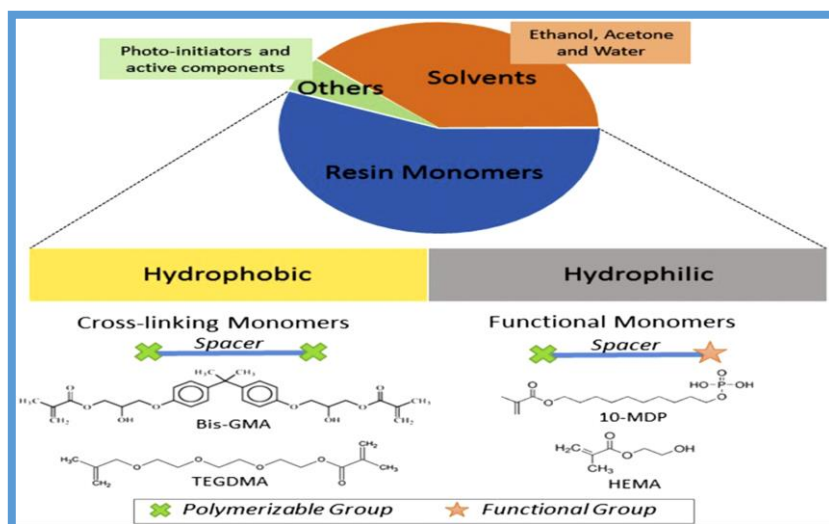


Figure 1-2: Composition of dental adhesives and examples of cross-linking and functional monomers used in contemporary adhesive systems (Bedran-Russo *et al.*, 2017).

UNIVERSAL ADHESIVES

Although there is no official definition for the ‘Universal Adhesives’, literature describes it as a one-bottle, no-mix adhesive agent that performs equally well with any adhesion strategy used (Alex, 2015). The term “Universal” reflects manufacturer’s claims that such adhesives can be utilized with any adhesion strategy according to each specific clinical situation and offer the versatility of use with a different direct and indirect restorative materials (Zhang *et al.*, 2016; Nagarkar *et al.*, 2019).

The main difference between conventional one-step self-etch adhesives and universal adhesives is that most universal adhesives are based on 10-MDP (and/or other monomers) (Kaczor *et al.*, 2018; Perdigao *et al.*, 2019). Most universal adhesives fall under the ultra-mild ($\text{pH} \geq 2.5$), mild ($\text{pH} \approx 2$) and intermediately strong (pH between 1-2) categories (Nagarkar *et al.*, 2019; Papadogiannis *et al.*, 2019).

The 10-MDP based universal adhesives can chemically bond to the hydroxyapatite crystals of dentin through electrostatic interactions by ionic bonds with the calcium ions of the hydroxyapatite crystals, resulting in a stable insoluble MDP-calcium salt. Moreover, the phosphate groups in MDP form covalent bonds with the corresponding phosphate groups of hydroxyapatite crystals to form insoluble salts. The continual deposition of successive layers of 10-MDP- Ca^{+2} salts on the outer surface of the hydroxyapatite crystal is a process called ‘nano-layering’ (**Perdigao *et al.*, 2019**).

Laboratory bond strength tests showed that the chemical bonding formed by 10-MDP- Ca^{+2} salt is more stable in water than that formed from monomers such as 4-META and phenyl-P (**Elkaffas *et al.*, 2018**). However, the presence of HEMA may hamper the chemical bonding ability of 10-MDP-containing universal adhesives, because it negatively affects the formation of MDP-Ca salts (**Van Meerbeek *et al.*, 2020**).

The active application (rubbing) of 10-MDP-containing universal adhesives results in more intense nano-layering than passive application (**Alex, 2015; Zhang *et al.*, 2016**). Such active application results in higher bond strengths to enamel when compared to passive application. These improvements from rubbing the adhesive on the bonding substrate may be caused by higher concentration of 10-MDP molecules in intimate contact with hydroxyapatite, also it may related to higher solvent evaporation rate from the enamel and dentin surfaces (**Costa *et al.*, 2017; Nagarkar *et al.*, 2019**).

Differences in the hydroxyapatite structure in dentin and enamel affect the pattern of interaction of 10-MDP with such substrates (**Elkaffas *et al.*, 2018**). The lesser amount and smaller hydroxyapatite crystals of dentin, and their criss-cross orientation in comparison to the more parallel orientation in that of enamel makes dentin more receptive to the chemical interaction with 10-MDP. Such interaction discloses the formation of a nano-layered structure, which is less in enamel than in dentin (**Chen *et al.*, 2016; Van Meerbeek *et al.*, 2020**).

CONCLUSIONS

Recent developments in dentistry have produced adhesive integrated materials (such adhesive systems and composites) and techniques focused at restoring the natural tooth appearance, particularly in the anterior section, in response to rising requests for cosmetic restorative treatments (97). The ability to obtain a perfect color match with natural teeth and the stability of the optical qualities over time are the essential requirements for adhesive aesthetic materials. In order to achieve morphologic, optical, and biologic results that mimic natural enamel and dentine, dental restorations are intended to be aesthetically pleasing. In order to achieve harmony with the nearby anatomical structures, color matching is done.

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