

Self-Etch Adhesive Systems: A Review

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Abstract

Adhesive dentistry has evolved rapidly since it was introduced. Effective bonding to two hard tissues of different nature is the main challenge for dental adhesives. Bonding to enamel has been proven to be durable while bonding to dentin has always been challenging. Current adhesive systems rely on two major means for a reliable bonding to the tooth structure. The first method is etch and rinse technique in which the smear layer is removed completely and demineralization of subsurface is seen by etching with acids. The second method is self-etch adhesive system which uses the smear layer as bonding substrate. Self – etch adhesive systems have simpler adhesive protocols. This article reflects the general characteristics, history, classification and bonding mechanism of self-etch adhesive systems.

Keywords: Bonding, Dentin, Enamel, Self-etch adhesive.

Introduction

Bunocore introduced acid-etch technique in 1955.^[1] Adhesion to dentin has always been challenging due to its heterogenous composition with much higher organic and water content than enamel. The inorganic composition of

dentin, the mesh of collagen, humidity and its relation with the pulp tissue makes it the real “Achilles heel” of adhesive dentistry.^{[2],[3]}

The basic mechanism of adhesion between tooth substrate and bonding agents is based on an exchange process. Fundamental mechanism for retention of resin-based composite restorations is entanglement of resin monomers with dental substrates, or hybridization for bonding of etched enamel and dentin.^{[4],[5]}

Self-etching adhesives were introduced to simplify the bonding steps and reducing the actual bonding time. The resin monomers penetrate the whole depth of the demineralized dentin as etching and priming of the dentin surface is done in the same step,. Incomplete resin penetration to this depth will lead to an exposed demineralized dentin zone at the base of the hybrid layer.

Elimination of demineralized dentin zone from the bond structures is important to increase the bond longevity for the adhesive restorations.^[6]

History

The concept of self-etch approach came approximately 20 years ago, however, as no acid etching/rinsing or conditioning steps were used in the first and second generations of bonding agents so they can be considered self-etch materials. They used to contain glycerophosphoric acid dimethacrylate, halophosphorous ester-based primers of Bis-GMA or HEMA, which were used to be applied to unconditioned dentin.^{[7],[8]}

The first commercially available system contained 2-(methacryloyloxyethyl)phenyl hydrogenphosphate (Phenyl-P) as main acidic monomer. Chemical bond is formed between the functional group of this monomer to hydroxyapatite.^{[9],[10]} An aqueous solution of acidic functional monomers, with a pH relatively higher than that of phosphoric acid etchants is the basic composition of self-etch primers and self-etch adhesive systems. Water provides the medium for ionization and action of these acidic resin monomers.

Self-etch adhesive systems also contain HEMA monomer to increase the wettability of dentin surface because most of the acidic monomers are low water-soluble. Bi- or multi-functional monomers provide strength to the cross-linking formed from monomeric matrix.^[11] Self-etch adhesives have advantages over conventional etch-and-rinse systems, such as less postoperative sensitivity and technique sensitivity. Simultaneous infiltration of adhesive during self-etch process, is also an advantage of self-etch adhesives.^{[12]-[15]}

By increasing the acidic monomer concentration the adhesive solution becomes more hydrophilic and simplify the bonding procedure into one step. However, the resin-dentin bond has been compromised with the increase in acidic monomer concentration as it forms a semi-permeable hybridization. The dentinal sealing is also compromised by a more water permeable hybrid layer

which results in the premature degradation of resin-dentin bonds and ultimately of the restoration.

Classification

The current self-etch adhesive systems are classified on the basis of number of clinical application steps: one-step or two-step adhesives.^[15] In two-step self-etch adhesive systems, a hydrophilic etching primer which combines acidic monomers simultaneously etch and prime tooth substrate^{[10],[11]}, and then after solvent evaporation, a layer of hydrophobic and bonding agent seal the dentin¹⁸ while in one-step self-etch adhesive systems or all-in-one adhesives etching, priming and bonding are combined^[21], thus containing acidic functional monomers, hydrophilic and hydrophobic monomers, water and organic solvents into a single solution^[22]. One-step self-etch adhesive systems are also called “Universal or Multi-mode Adhesives”, which can be applied in etched or unetched enamel and dentin.

The etching aggressiveness of self-etch adhesive systems can also be classified on the basis of acid dissociation constants (pKa values) into: “strong” (pH<1) “intermediately strong” (pH≈1.5), “mild” (pH≈2) and “ultra-mild” (pH≥2.5)^[23]. “Strong” self-etching shows good bonding performance on enamel^{[24],[25]}, while “mild” self-etching on enamel is not efficient and can be improved by prior phosphoric acid etching.^{[26],[27]} However, at dentin, “strong self-etching” dissolves nearly all smear layer, but does not remove the dissolved calcium phosphates. These embedded calcium phosphates seem to have low hydrolytic stability, with non-stable chemical interaction with the exposed collagen which causes weakening of the interfacial integrity, especially in a long-term.^[15] “Intermediate strong” self-etching is a transition between “strong” and “mild” etching characteristics of the hybrid layer with demineralized top layer and partially demineralized base.^[13] “Mild” self-

etching partially removes the smear layer, resulting a thin hybrid layer. It has advantage of leaving substantial amount of hydroxyapatite-crystals around collagen fibrils, which may establish chemical bond with specific carboxylic or phosphate groups of functional monomers.^[28] The 'ultramild' self-etching can only expose superficially dentin collagen creating a nanometer interaction zone.^[29] The smear layer thickness of the self-etch adhesive systems can provide good information, however their relationship with bonding performance is controversial.^{[30]-[32]}

Bonding mechanism to enamel and dentin

The chemical formulation of current self-etch adhesive systems, specifically the functional monomers play an important role on the long-term bonding performance of bonding systems. Adhesive monomers replace minerals from the hard tissues of teeth which create an effective micromechanical interlock after polymerization.^[13] Enamel etching with phosphoric acid before the application of bonding agent is the standard procedure for better bonding.^[33]

The formation of a homogenous and compact hybrid layer is important for the bonding stability to dentin. Hydrolysis and proteolytic breakdown of the collagen fibril components of the hybrid layer or hydrolytic degradation of the hybrid layer's adhesive components is the major cause of degradation of the dentin bonding interface.^{[2],[34]} Self-etch adhesives demineralize the dentin to ensure a more complete resin infiltration.^[35]

The bonding mechanism of self-etch adhesive systems has been described by two-fold bonding mechanisms; micro-mechanical interlocking and chemical bonding. The micro-mechanical bonding provides strength against mechanical stress, while the chemical interaction decreases hydrolytic degradation, restoring the marginal sealing of restorations for a longer period.^{[14],[15],[21],[25]} The

functional acidic monomers chemically interact with hydroxyapatite. They contain specific carboxylic, phosphonic or phosphate groups, such as: Phenyl-P, 10-methacryloyloxydecyl dihydrogenphosphate(10-MDP), methacryloyloxy dodecyl pyridinium bromide (MDPB), 4-methacryloyloxy ethyl trimellitate anhydride(4-META), 4-methacryloyloxy ethyl trimellitic acid (4-MET), 11-methacryloyloxy-1, 1-undecanedicarboxylic acid (MAC-10), 4-acryloyloxy ethyl trimellitate anhydride (4-AETA), 2-methacryloyloxy ethyl dihydrogen phosphate (MEP), phosphate methacrylates, acrylic ether phosphonic acid and other phosphoric acid esters.^[11] The 4-MET acts as a demineralizing agent and an adhesion promoting monomer as it contain carboxylic groups attached to the aromatic group.

The two carboxylic groups are related to demineralizing properties and monomer infiltration, while the aromatic group provides the hydrophobic characteristics which reduces the acidity and the hydrophilicity from carboxyl groups. Ca-4MET salt is formed by an ionic bond between calcium in hydroxyapatite with 4-MET monomer. Water is added to 4-META crystalline powder to obtain 4-MET by hydrolysis reaction. 4-AETA monomer contains an acrylate polymerizable group. The acrylate group which provides better polymerization reaction than methacrylate group in 4-META.^[36] The MAC-10 monomer is considered hydrolytically stable because its spacer group have 10 carbons atoms which makes this monomer with hydrophobic properties. The dihydrogen phosphate group from 10-MDP monomer is responsible for etching and chemical bonding, while the hydrophobic properties and hydrolytic stability to this acidic monomer is provided by its long carbonyl chain. The pyridinium bromide group of MDPB monomer has antibacterial effects against bacteria by direct contact bacteriolysis. This antibacterial group is positively

charged and destroys the negatively charged cell membrane concentrations of the bacteria.^{[37]-[39]}

Discussion

Sano et al^[40] states that the degree of demineralization is often greater than the penetration of adhesive resins resulting in a void and a non-hybridized demineralized zone which can lead to microleakage, decreased bond strength and post-operative sensitivity. da Silva et al^[41] investigated biological compatibility of different adhesive systems and showed that most of the tested adhesive presents a certain degree of toxicity, inducing apoptosis or interfering with the cell cycle which also interferes in dentin regeneration. They also observed that although the remaining dentin promotes a pulp capping in deep cavities, this protection is not sufficient to prevent penetration of residual monomers.

Van Landuyt et al^[42] stated that self etch adhesive bonding agents decreased the bond strength to dentin after immersion in water for 6 months and also observed that self-etch adhesives failed often under hybrid layer at dentin. These failures have been linked to insufficient encapsulation of the surface smear layer. In vitro studies have indicated the selective enamel etching for bonding of self-etch adhesive systems^{[43]-[46]}, while other studies observed that the retention rate of composite restorations was not influenced by selective enamel etching in non-carious Class V lesions.^{[47]-[50]}

Khaldoan H. Alshaikh et al^[51] conducted a metaanalysis to quantify the effects of some surface pretreatment methods on the bonding of self-etch adhesives to dentin. They concluded that dentin surface pretreatment with deproteinizing agents does not enhance the bonding of self-etch adhesives to dentin. The HOCl deproteinizing agent has minimal adverse effects in comparison with NaOCl solutions on bonding to dentin. The chemistry of one-step self-etch systems is very challenging. The

incorporation of hydrophilic and hydrophobic monomers, along with organic solvents and water into a single bottle leads to high hydrophilicity of these systems. Hydrophilic chemistry creates permeable membranes which causes water diffusion from the underlying dentin across the adhesive layer.^[52] These simplified self-etch systems are more prone to water sorption which causes water swelling and reduces frictional forces between the polymer chains in a process known as plasticization. This water-driven process can decrease the mechanical properties of the polymer matrix.^[53]

Feilzer et al^[54] reported that the ratio of the bonded to unbonded surfaces within the preparation, the configuration (C) factor, can be used to predict which restorations are most likely to have bond failures between the resin and the tooth. They stated that restorations with a C-factor less than one are more likely to survive polymerization contraction stresses and remain bonded to the tooth. This may be a problem, because Class I preparations have a mean C-factor of 4.03 and Class II preparations have a mean C-factor of 1.85.^[55] He et al^[56] supported the negative effect of C-factor and reported that bulk filling a cavity with a C-factor of five produced the lowest bond strength and more microleakage has been observed as the C-factor increases.^{[57],[58]} An in vivo study has also reported that the resin-dentin interdiffusion zone was detached from the overlying resin in restorations with a C-factor of five.^[59]

Conclusion

Modern adhesive dentistry allows conservation of hard tissue to facilitate effective and efficient restoration. The goal of adhesive dentistry is to obtain an adequately strong bonding of restorative resin to tooth for appropriate retention, reduced microleakage and thus providing superior color stability and clinical longevity of restoration.

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