

Self-Etch Adhesive Systems: A Literature Review

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This paper presents the state of the art of self-etch adhesive systems. Four topics are shown in this review and included: the historic of this category of bonding agents, bonding mechanism, characteristics/properties and the formation of acid-base resistant zone at enamel/dentin-adhesive interfaces. Also, advantages regarding etch-and-rinse systems and classifications of self-etch adhesive systems according to the number of steps and acidity are addressed. Finally, issues like the potential durability and clinical importance are discussed. Self-etch adhesive systems are promising materials because they are easy to use, bond chemically to tooth structure and maintain the dentin hydroxyapatite, which is important for the durability of the bonding.

Introduction and History of Self-Etch Adhesive Systems

The concept of self-etching approach was created approximately 20 years ago, however, the first and second generations of bonding agents can be considered self-etch materials because no acid etching/rinsing or conditioning step were used. These early generations of dentin adhesives used glycerophosphoric acid dimethacrylate, halophosphorous ester-based primers of Bis-GMA or HEMA, which were applied to unconditioned dentin (1,2). The first commercially system contained as main acidic monomer the 2-(methacryloyloxyethyl)phenyl hydrogenphosphate (Phenyl-P). The monohydrogenphosphate group of this functional monomer was responsible for preparing the enamel and dentin for chemical bonding of this functional group to hydroxyapatite (3,4).

The basic composition of self-etch primers and self-etch adhesive systems an aqueous solution of acidic functional monomers, with a pH relatively higher than that of phosphoric acid etchants. The role of water is to provide the medium for ionization and action of these acidic resin monomers. Self-etch adhesive systems also contain HEMA monomer because most of the acidic monomers are low water-soluble and to increase the wettability of dentin surface. Bi- or multi-functional monomers are add to provide strength to the cross-linking formed from monomeric matrix (5).

Because self-etch adhesive systems do not require a separate acid conditioning step and moist post-rinse control, they are considered simplified adhesive materials. They offer some advantages over conventional etch-and-rinse systems, such as reduction of postoperative sensibility

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and less sensitive technique. Another advantage is that infiltration of adhesive resin tends to occur simultaneously with the self-etch process, although there are some controversial (6-9).

To simplify the bonding procedure into one step, the adhesive solution became more hydrophilic because the increasing of acidic monomer concentration. However, the increase in acidic monomer concentration in self-etch adhesive systems has compromised the resin-dentin bond, since a semi-permeable hybridization is formed. A more water-permeable hybrid layer also compromises the dentinal sealing, which results in the premature degradation of resin-dentin bonds and consequently of the restoration (10-14).

Characteristics and Properties

Dental adhesive technology has evolved in the past decades toward complex formulations with simplified clinical procedures. The demand for reduced technique-sensitivity, shorter clinical application time and less incidence of post-operative sensitivity have made self-etch adhesive systems a promising approach when compared to the etch-and-rinse systems (7,15).

The current self-etch adhesive systems are classified based on the number of clinical application steps: one-step or two-step adhesives (9). Two-step self-etch adhesive systems include the use of a hydrophilic etching primer, which combines acidic monomers that simultaneously etch and prime tooth substrate (3,4), and after solvent evaporation, a layer of hydrophobic and bonding agent seal the dentin (12). One-step self-etch adhesive systems are all-in-one adhesives, which combine the etching,

priming and bonding (16), thus containing acidic functional monomers, hydrophilic and hydrophobic monomers, water and organic solvents into a single solution (17). There are one-step self-etch adhesive systems called "Universal or Multi-mode Adhesives", which can be applied in etched or unetched enamel and dentin (Figs. 1A and 1B). These bonding agents are also indicated to be used as silane for glass ceramics and primers for metal alloys and polycrystalline ceramics. The longevity and strength of these bonds to tooth and prosthetic materials have been studied and will show if these adhesives are effective in all of these types of surfaces (18,19).

Depending upon the acid dissociation constants (pKa values), the etching aggressiveness of self-etch adhesive systems can also be classified into: "strong" (pH<1) "intermediately strong" (pH≈1.5), "mild" (pH≈2) and "ultra-mild" (pH≥2.5) (20). Indeed, the more aggressive systems, deeper demineralization of the tooth substrate (Fig. 2) occurs resembling that of phosphoric acid-etching treatment (Fig. 3) (6). At enamel, "strong" self-etching shows good bonding performance (21,22), while the bonding effectiveness of "mild" self-etching on enamel is not efficient and can be improved by prior phosphoric acid etching (23,24).

On the other hand, 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, thereby weakening the interfacial integrity, especially in a long-term (9). "Intermediate strong" self-etching shows a transition between "strong" and "mild" etching characteristics of the hybrid layer formed. It has typically a hybrid layer with demineralized top layer and partially

demineralized base (7). "Mild" self-etching partially removes the smear layer, forming a thin hybrid layer (Fig. 4). It has the great 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 (25). The 'ultra-mild' self-etching can only expose superficially dentin collagen, producing a nanometer interaction zone (26). The smear layer thickness of the self-etch adhesive systems can provide good information, however their relationship with bonding performance is controversial (27-29).

Several laboratory tests are commonly used to evaluate the bonding performance of adhesives, such as micro-tensile (30) and micro-shear (31) bond strength tests. When the components at the bonding area, such as filling material, bonding resin, hybrid layer and underlying dentin are bonded and connected strongly enough to each other, the bond strength is determined by the mechanical strength of components. The weakest part should be fractured during the test. In this context, evaluation of mechanical strengths of interfacial components is considered to correlate with the bond-strength (32).

Mechanical properties such as hardness and Young's modulus of successive layers across a resin-dentin bonding area can be measured by nanoindentation testing (33). Hardness measured at demineralized dentin along with the adhesive resin layer area seems to be lower than compared with unaltered dentin (34). Sufficiently flexible resin layer could resist the polymerization shrinkage stress of the restorative composite (35), thus maintaining the bonding performance. Moreover, Young's modulus seems to be dependent of hydroxyapatite content, which presence may induce spontaneous polymerization of self-etch adhesive systems (36). Nanoindentation and bond-strength testing

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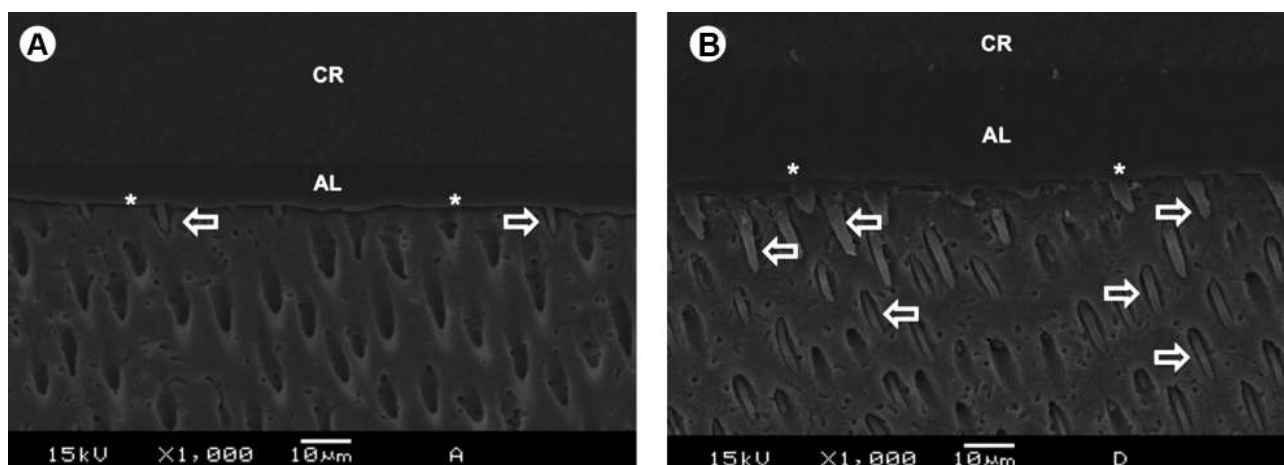


Figure 1. SEM micrographs of the resin-dentin interface bonded with the one-step self-etch mode (Fig. 1A) and etch-mode (Fig. 1B) Scotchbond Universal adhesive. Figure 1A shows a thin hybridized layer (*) and few/short resin tags (arrow). Figure 1B shows that thickness of dentin hybridized layer (*) was approximately 3.0 to 4.0 mm (AL: adhesive layer, CR: composite resin, arrows: indicate resin tags, 1,000x magnification).

on different self-etch adhesive systems suggested that when properly handled, two-step self-etch adhesive may perform better than one-step self-etch adhesive and that air-drying is a crucial step during the application of a solvent containing adhesive (37).

Due to the components of self-etch adhesive systems, water sorption and solubility of the bonding resin itself are significant factors for the mechanical properties of the bonding layer (32). Besides the number of application steps or etching aggressiveness, their bonding performance seems to be rather material-dependent. The chemical formulation of current self-etch adhesive systems, in specific the functional monomers, certainly plays an important role for the adhesive long-term bonding performance.

Bonding Mechanism to Enamel and Dentin

The bonding mechanism of self-etch adhesive systems has been intensely investigated and two-fold bonding mechanisms; micro-mechanical interlocking (Figs. 1A, 2 and 4) and chemical bonding were described, which seems to be advantageous in terms of restoration durability. The micro-mechanical bonding contributes to provide strength against mechanical stress, while the chemical interaction reduces hydrolytic degradation, keeping the marginal sealing of restorations for a longer period (8,9,16,22).

The functional acidic monomers are able to chemically interact with hydroxyapatite and are composed by specific carboxylic, phosphonic or phosphate groups, such as:

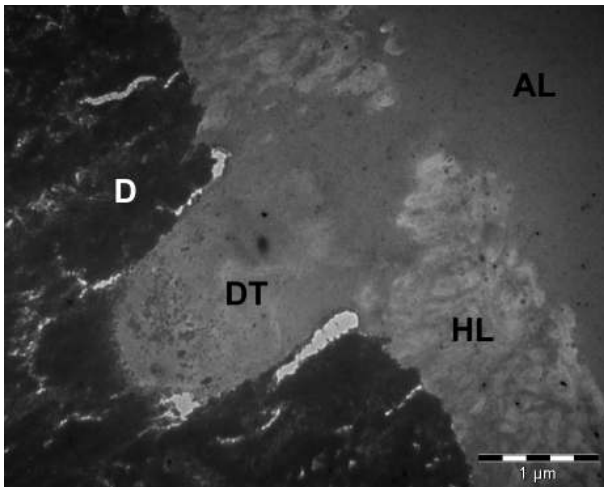


Figure 2. TEM micrograph of the resin-dentin interface bonded with the one-step self-etch adhesive Futura Bond NR. Thickness of hybridized layer (HL) was approximately 1.2 μm (AL: adhesive layer, D: dentin, DT: dentin tubule, 7,000x magnification).

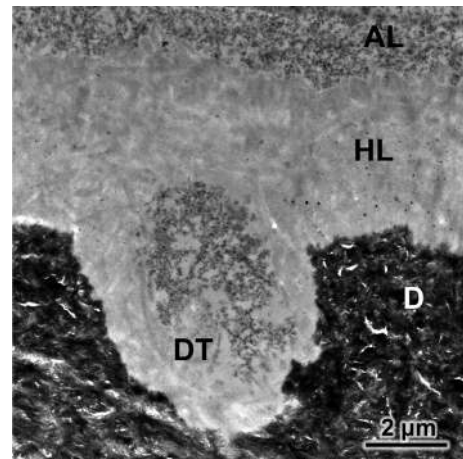


Figure 3. TEM micrograph of the resin-dentin interface bonded with the etch-mode of Scotchbond Universal. The thickness of hybrid layer (HL) formed after phosphoric acid etching and adhesive application was approximately 4 μm (AL: adhesive layer, D: dentin, TD: dentin tubule, 10,000x magnification).

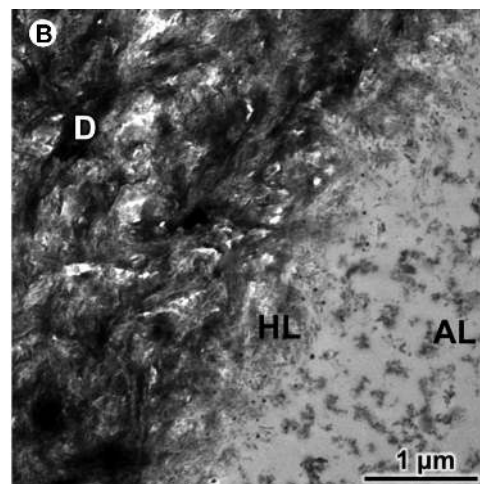
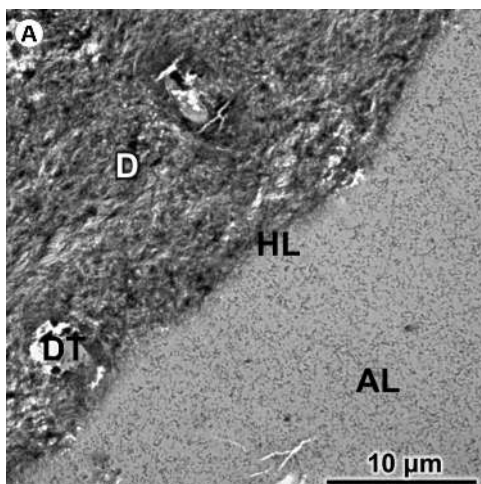


Figure 4. TEM micrographs of the resin-dentin interface bonded with the two-step self-etch primer Clearfil SE Bond. The high magnification showed that the thickness of interaction zone (HL) was less than 1.0 μm (AL: adhesive layer, D: dentin, DT: dentin tubule, 3,000 x and 30,000x magnification, respectively).

Phenyl-P, 10-methacryloyloxydecyl dihydrogenphosphate (10-MDP), methacryloyloxydodecylpyridinium bromide (MDPB), 4-methacryloyloxyethyl trimellitate anhydride (4-META), 4-methacryloyloxyethyl trimellitic acid (4-MET), 11-methacryloyloxy-1,1-undecanedicarboxylic acid (MAC-10), 4-acryloyloxyethyl trimellitate anhydride (4-AETA), 2-methacryloyloxyethyl dihydrogen phosphate (MEP), phosphate methacrylates, acrylic ether phosphonic acid and other phosphoric acid esters (5).

The 4-MET acts as demineralizing and an adhesion-promoting monomer due to the 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 tends to reduce the acidity and the hydrophilicity from carboxyl groups. 4-MET monomer is able to form an ionic bond with calcium in hydroxyapatite, resulting Ca-4MET salt. To obtain 4-MET by hydrolysis reaction, water is added to 4-META crystalline powder and when used with methyl methacrylate (MMA), they form the 4-META/MMA-TBB (tri-n-butyl borane) adhesive (38-41).

4-AETA monomer contains an acrylate polymerizable group instead of a methacrylate group found in 4-META monomer. The acrylate group of 4-AETA provides better polymerization reaction than methacrylate group (42). The MAC-10 monomer is considered hydrolytically stable because its spacer group containing 10 carbons atoms. This number of carbons atoms at spacer group makes this monomer with hydrophobic properties. Two-methacryloyloxyethyl dihydrogen phosphate (MEP), phosphate methacrylates, acrylic ether phosphonic acid and phosphoric acid esters are found in specific bonding agent brands (5).

The dihydrogenphosphate group from 10-MDP

monomer is responsible for etching and chemical bonding, while its long carbonyl chain provides the hydrophobic properties and hydrolytic stability to this acidic monomer. 10-MDP forms a strong ionic bond with calcium from hydroxyapatite of enamel or dentin, also resulting in Ca-salt (41). 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 cell membrane concentrations of the bacteria, which are generally negatively charged (43-45). MDPB at high kills the planktonic forms and biofilms of *S. mutans* cells in a short time period (60 s), and at low concentrations, it inhibits lactate dehydrogenase metabolic enzymatic activity (46).

Amide monomers in experimental adhesives have been studied, according to reaction between amide groups of the monomer with the carboxyl groups of collagen by hydrogen bonds. The chemical modification to synthesize this monomer is the presence of amide group instead of an ester group as in conventional acrylates and methacrylates-based adhesives. An important advantage is that acrylamides provide better hydrolytic resistance as compared to the ester groups. The adhesives containing amide monomers should be specific for dentin, which contain the amino acids from collagen available for bonding (47-49).

Although *in vitro* studies have indicated the selective enamel etching for bonding of self-etch adhesive systems(50-53), other studies demonstrated that the retention rate of composite restorations was not influenced by selective enamel etching in non-carious Class V lesions (54-56). Because the phosphoric acid etching, it is possible to observe the penetration of resin tags into conditioned enamel (Figs. 5A and 5B), which tends to increase the bond strength, however controversial still remain in this issue.

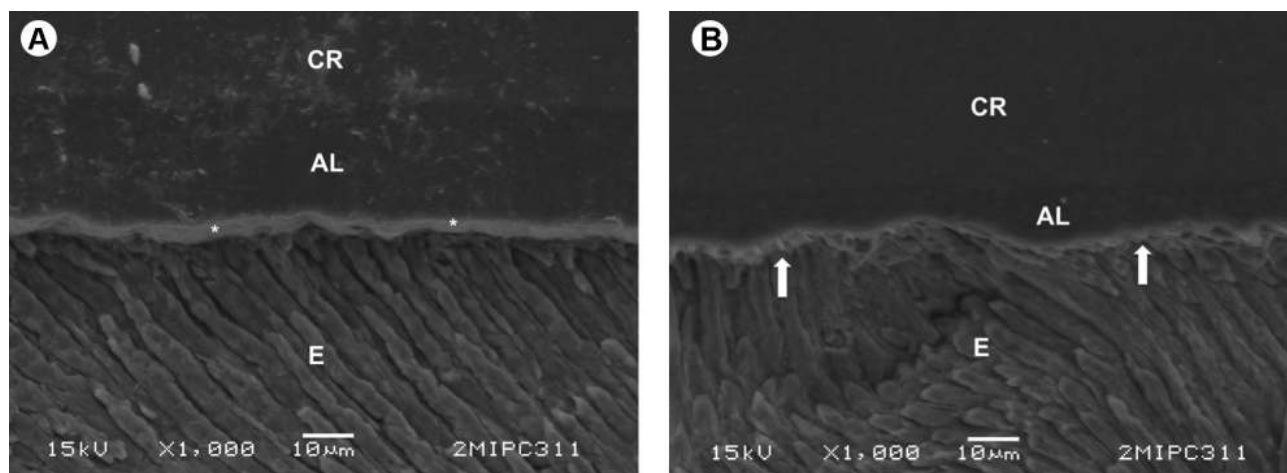


Figure 5. SEM micrographs of the resin-enamel interface bonded with the one-step self-etch mode adhesive Scotchbond Universal (Fig. 5A). Asterisks show the bonded area. The Figure 5B is a SEM micrograph of the resin-enamel interface bonded with the three-step etch-and-rinse adhesive Optibond FL. Arrows show resin tags and the bonded area (CR: composite resin, AL: adhesive layer, E: enamel, 1,000x magnification).

Creating ABRZ at Enamel/Dentin-Adhesive Interface

Secondary caries is considered as a major cause for the failure of restorations. Acidic bacterial byproducts may infiltrate not only the bonding interface, but also the tooth tissue at the periphery, creating a marginal demineralized zone, and thus rapidly promote caries occurrence. In this regard, it has been suggested that an increased resistance of the tooth-resin interface to acid may effectively retard the progression of secondary caries (57).

SEM observation at dentin-adhesive interfaces reported the presence of an acid-base resistant zone (ABRZ) beneath the hybrid layer in self-etch adhesive systems after acid-base challenge (Fig. 6) (58). Because this layer can resist acid and base challenges, it might play an important role in the prevention of secondary caries. It has been shown that morphology of dentin ABRZ was highly adhesive-material dependent and that ABRZ formed in self-etch adhesive

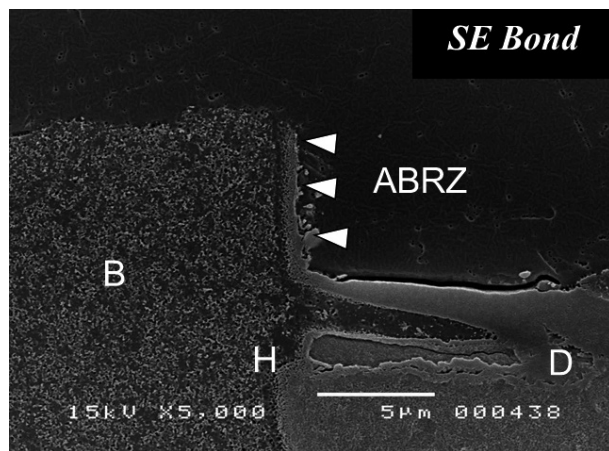


Figure 6. SEM image of the dentin-adhesive interface after acid-base challenge. The acid-base resistant zone (ABRZ) was observed beneath the hybrid layer in a two-step self-etch adhesive system (5,000x magnification).

systems but not in etch-and-rinse adhesive systems (Fig. 7) (59-64). Under transmission electron microscopy (TEM), selected area electron diffraction (SAED) is a crystallography method that provides information on the local crystalline structure of thin sections. The TEM/SAED evidence demonstrated that the ABRZ contained densely arranged apatite crystallites that had different characteristics from the hybrid layer (Fig. 8) (60,65).

Although the formative mechanism is still unclear, it was assumed that the penetration of the monomers into the tooth tissue beyond the hybrid layer and the chemical interaction between the functional monomer and hydroxyapatite may contribute to the formation of ABRZ. With regard to the ABRZ concept, it is recommended to avoid complete demineralization of dentin by using phosphoric acid, as the procedure compromises complete infiltration of monomers and reduces the chance of an effective chemical bonding and protection of apatite against acid-attack (65).

It has been shown that some functional monomers in self-etch adhesive can chemically interact with the hydroxyapatite in the demineralized tooth layer within a clinically manageable time (5,41,66-69). MDP molecule has a long linear alkyl chain and phosphoric acid ester group. MDP has been found to interact chemically with hydroxyapatite intensively and stably (Yoshida et al., 2004). In contrast, Phenyl-P contains a shorter alkyl chain spacer and a phenyl group at the acidic moiety. The chemical bonding capacity of Phenyl-P is very limited.

Enamel has a higher mineral content with a matrix structure different from dentin collagen network. For enamel bonding substrate, it was reported the formation of ABRZ with a two-step self-etch adhesive system, Clearfil SE Bond (Kuraray Noritake Dental, Tokyo, Japan), which contains MDP as the acidic functional monomer (Fig. 9). The enamel ABRZ is not below the hybrid layer, but it is rather

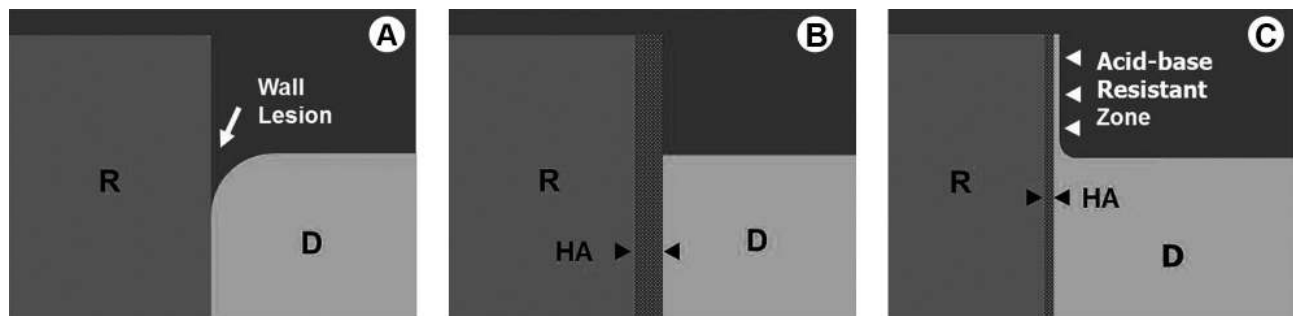


Figure 7. Schematic summary of the results of acid-base challenge, where: For no treatment on dentin, no hybrid layer formation was observed, but wall lesion was found. Wall lesion formation suggested that the interface could not resist acid-base challenge, hence causing secondary caries formation in clinical situations. For acid-etching systems, a hybrid layer was observed, but the acid-base resistant zone and wall lesion were not detected. For self-etch systems, a hybrid layer was observed and the acid-base resistant zone was observed beneath the hybrid layer, which was along the dentin-adhesive interface.

at the interface, which was not dissolved after the acid-base challenge (70). However, in the experimental adhesive system containing Phenyl-P, which was substituted for MDP, the enamel ABRZ could not be distinguished at the most parts of the corresponding region. And a funnel-shaped erosion area was noted at the junction of ABRZ in this group, indicating a weak area vulnerable to acid-base attack beneath the bonding interface.

On the mechanism of action of fluoride from adhesives, it has been suggested that the fluoride could enter calcium

phosphate rich spaces created by self-etch adhesive systems interact to prevent the future demineralization. A delta-shaped region of dentin ABRZ has been formed from the upper slope to the end of outer lesion when the fluoride-releasing two-step self-etch adhesive system, Clearfil Protect Bond (Kuraray Noritake Dental) was used (64). Another study showed that the interface created by a fluoride-releasing adhesive was more stable than that of a similar fluoride-free adhesive after long-term durability test of the dentin ABRZ (Fig. 10) (71). However, there was a minimum threshold for fluoride release to affect the acid-resistance of interfacial dentin using the experimental two-step self-etch adhesive systems with



Figure 8. TEM image of the dentin-adhesive interface after acid-base challenge. The TEM/SAED evidence demonstrated that the ABRZ contained densely arranged apatite crystallites (5,000x magnification).

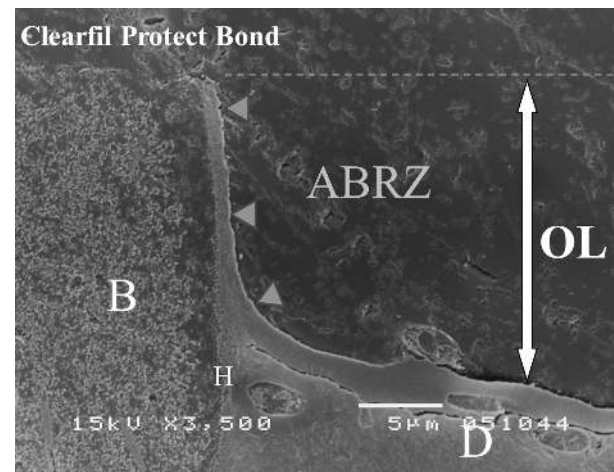


Figure 10. SEM image of the dentin ABRZ after long-term durability test. A delta-shaped region of dentin ABRZ was formed from the upper slope to the end of outer lesion when the fluoride-releasing two-step self-etch adhesive system; Clearfil Protect Bond. The interface created by the fluoride-releasing adhesive was more stable than that of a similar fluoride-free adhesive after 3-month immersion in distilled water (3,500x magnification).

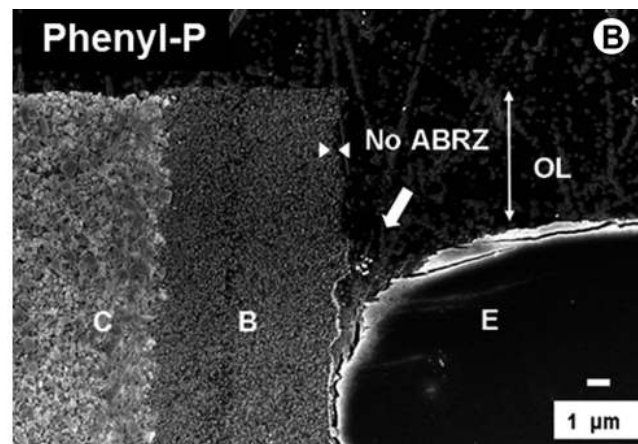
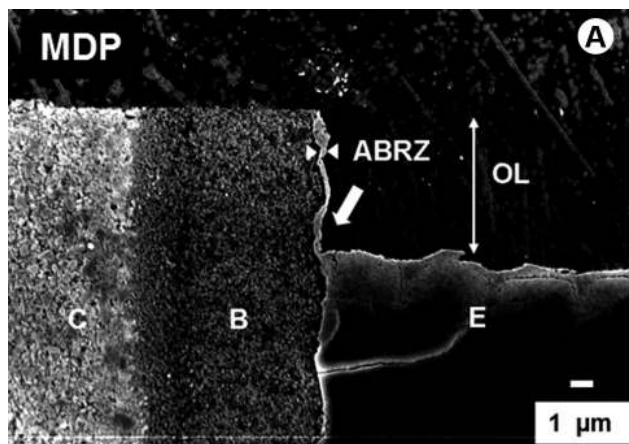


Figure 9. SEM images of the enamel-adhesive interfaces after acid-base challenge. The formation of enamel ABRZ with a two-step self-etch adhesive system, which contains MDP as the acidic functional monomer (left), while the enamel ABRZ could not be distinguished at the most parts of the corresponding region in the Phenyl-P-containing adhesive. And a funnel-shaped erosion area was noted at the junction of ABRZ in this group, indicating a weak area vulnerable to acid-base attack beneath the bonding interface (2,000x magnification).

different concentration of sodium fluoride (72).

The findings can explain favorable results obtained with MDP-based two-step adhesives in laboratory as well as clinical studies (20). The ABRZ pattern obtained from each adhesive system may become a good indicator to predict its bonding durability to tooth substrates. The interface exhibiting this property is a protected layer, which may bring up new discussions on dentin-bonding mechanisms and renew the classic hybrid layer concept (73).

Resumo

Este artigo apresenta o estado da arte de sistemas adesivos autocondicionantes. Quatro temas são apresentados nesta revisão: o histórico desta categoria de agentes de união, o mecanismo de adesão, as características/propriedades, e a formação da zona ácido-base resistente nas interfaces esmalte/dentina-adesivo. Além disso, as vantagens relativas aos sistemas de condicionamento total (*etch-and-rinse*) e as classificações dos sistemas adesivos autocondicionantes de acordo com o número de passos e acidez são abordados. Por fim, são discutidas questões como a durabilidade potencial e a importância clínica. Sistemas adesivos autocondicionantes são materiais promissores porque são fáceis de usar, unem-se quimicamente à estrutura do dente e preservam a hidroxiapatita dentinária, o que é importante para a durabilidade da ligação.

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