Enamel Acid Etching: A Review

Abstract

Bonding to enamel has over 50 years of history. Efforts have been made to develop or introduce a simplified alternative, but enamel acid etching remains the most effective procedure for stable enamel bonding. Although acid etching is considered the most popular procedure in dentistry, there are characteristics that deserve special attention because of how crucial they can be in many clinical situations. This article reviews some of these aspects of enamel bonding using the acid-etching technique.

Learning Objectives

After reading this article, the reader should be able to:

- discuss aspects of enamel bonding with the acid-etching technique.
- explain the characteristics of hard tissue.
- describe the current knowledge to overcome saliva contamination during bonding to enamel.

A clinician’s ability to bond a restoration to enamel has influenced changes in prosthetic and cavity preparations, restorative approaches for esthetic corrections, bonding techniques for orthodontic devices, and the treatment of caries.1-3

Bonding to dentin has been the objective of several studies over the last 2 decades.1-3 In the beginning, the research was to find an adhesive system that could interact with efficacy in dentin, and more recently, the research has focused on simplifying the systems.1-3 Because a major part of bonding procedures requires simultaneously treating enamel and dentin, it is important to understand that the foundation of enamel bonding strongly influenced the development of dental adhesive systems. This article will review some relevant aspects of bonding to enamel using the total-etch technique.

Tooth Enamel

Enamel is the hardest tissue in the human body. Its mineral portion is approximately 96% of its weight,4 the rest is organic components and water. The mineral elements include hydroxyapatite crystals, approximately 0.03 μm to 0.2 μm, surrounded by a thin film of firmly bound water.4 In prismatic enamel, which constitutes the main fraction, the crystals are densely grouped and arranged in 3 directions. With this arrangement, lengthy prisms (a diameter of about 5 μm) from the dentoenamel junction to near the outermost surface of enamel are formed (Figure 1). The prisms maintain their integrity and support because of their transverse arrangement, irregular morphology, and overlapping patterns. At the moment of enamel instrumenta-
maturation process that makes it more resistant to demineralization. This maturation consists of mineral deposition from oral fluids in interprism spaces that were previously filled with water. Because all hard tissue is in continuous ionic change with the environment, it could be expected that human enamel will respond to acid conditioning differently, depending on age and factors related mainly to saliva and diet. Further research should be carried out to verify whether enamel changes over time might have clinical relevance when acid etched.

**Acid-Etching Technique**

During the 32nd Annual Meeting of the International Association for Dental Research in 1954, Buonocore suggested that using 85% phosphoric acid solution resulted in an adhesion of acrylic resin to enamel that lasted 1070 hours to debond when stored in water. Similar to other conceptual and technologic innovations, this procedure was introduced in dentistry ahead of its time and only 10 years later the bonding mechanism was described. Bis-GMA based adhesive systems and composites were developed, and the first clinical application, as a pit-and-fissure sealant, was reported in the literature.

Chemical treatment by acid etching enhances the topography of enamel, changing it from a low-reactive surface (Figure 3) to a surface that is more susceptible to adhesion (Figure 4 and 5). The demineralization is selective because of the morphological disposition of the prisms. The difference of angulation of the prism crystals causes the acid to have higher demineralization potential at certain microregions. After cavitory instrumentation,
depending on the angulation of the prisms, demineralization can be greater at the prism head (Figure 4) or at the periphery (Figure 5). These features are respectively known as type I and type II acid-etching patterns. This feature is important in understanding the fundamentals of adhesion though it is not clinically relevant.

Acid etching removes approximately 10 µm of enamel surface and creates a morphologically porous layer (5 µm to 50 µm deep). The surface free energy is doubled, and as a result, the low-viscosity fluid resin contacts the surface and is attracted to the interior of these microporosities created by conditioning through capillarity (capillary attraction). Therefore, resin tags are formed into microporosities of conditioned enamel (Figure 6) that after adequate polymerization, provide a resistant, long-lasting bond by micromechanical interlocking with this tissue.

**Bonding to Enamel with Hydrophilic Primers**

In most clinical situations, the restoration is bonded to enamel and dentin. To interact with this intrinsically moist tissue, an adhesive system was needed that could diffuse under this condition. The introduction of hydrophilic primers has allowed for adequate bonding to dentin. The modern adhesive systems that use the total-etch technique combine the functions of primer and adhesive in 1 bottle, intended for application on moist dentin surfaces.

For this reason, most adhesive systems that use the total-etch technique have in their formulation low-viscosity hydrophilic monomers diluted in organic solvents with a high potential of volatilization (acetone, water, or a mixture of both) to displace the moisture of conditioned dentin. The primer components (eg, hydroxyethyl methacrylate [HEMA], bis-phenyl dimethacrylate [BPDM], 4-methacryloyloxyethyl trimellitate anhydride [4-META]) are called bipolar because they have 2 functional groups (hydrophilic and hydrophobic). The hydrophilic end has the ability to interact even under moist conditions, and the hydrophobic end has chemical affinity with the methacyrylate group of the bonding resin matrix (also called hydrophobic adhesive) or with the composite resin.

Regarding bonding to enamel, the rapid volatilization of the solvent allows for the complete interdiffusion of the adhesive system through the extension of the conditioning, with a more intimate contact of the composite resin to enamel, which results in high bond strengths to this tissue and adequate marginal sealing, even in moist conditions.

It is not an easy procedure to keep dentin moist and dry only the enamel. It is possible that acetone-and ethanol-based solvents, included in mostly 1-bottle adhesives, remove residual moisture and promote a superior flow of the restorative material to acid-etched enamel. Hydrophilic primers become essential when enamel is moist and work very well when enamel is dry. However, because the presence of residual moisture and organic solvents interferes negatively in the complete polymerization of monomers, it is important after the application to properly dry with air spray of a triple syringe. Also, it has been theorized that the stability of bonding to enamel is also compromised with time because of the formation of adhesive layers similar to semipermeable membranes.

Isolating the operator field is important to achieve a contaminant-free working area. There is a lack of clinical evidence that says that bonding procedures with the use of rubber dam isolation results in better clinical performance than relative isolation, but it has been the authors’ experience that rubber dam isolation should be preferred to relative isolation because of the interference of patients’ breath moisture. A recent study simulating the oral environment compared the bond strength of bonding agents (hydrophilic and hydrophobic) to enamel under temperature and air humidity conditions of the oral cavity (35°C, 90% to 95% of relative humidity). The simulated contamination with high levels of air moisture did not compromise the bonding to enamel, whether it was accomplished with hydrophilic primer or a hydrophobic adhesive.

**Viscosity of the Adhesive System**

Some adhesives have inorganic filler particles to increase their film thickness and cohesive strength (filler loading ranges between 8.5% and 25% weight, depending on the brand). It seems that an intermediary flexible zone allows for a better transmission of the interfacial stresses induced by masticatory forces, differences in modulus of elasticity, water sorption presented by composite resins, and polymerization shrinkage. Filled sealants and flowable composite resins can bond to conditioned enamel without an intermediary adhesive agent. However, it has been reported that highly viscous sealants have greater dif-
ficulty penetrating enamel as much as the conditioning depth. Studies have demonstrated that filled adhesive systems present lower bond strengths to enamel, which seems to be related to the high viscosity of these adhesives. This seems to be related to the high viscosity of these adhesives, which makes it difficult to penetrate in interprismatic areas as deeply as unfilled adhesives. Adhesive systems containing nanofillers have been developed (Prime & Bond NT®, Adper Single Bond 2®). The nanofillers are designed to reinforce resin tags and the adhesive layer, and it seems that the low molecular weight does not compromise the interdiffusion in conditioned enamel.

Concentration of the Conditioner

When the acid-etching technique was extended to dentin (total-etch technique), the manufacturers included low concentration acid conditioners in adhesive systems possibly because of lack of information, knowledge, or marketing strategy, which supposedly would cause less aggression to pulpal tissue. In the early 1990s, it was common to find etchants such as 10% phosphoric acid, 10% maleic acid, 10% citric acid, 2.5% oxalic acid, and 2.5% nitric acid. Some of these acids do not result in a dull, frosty-white appearance typical of conditioned enamel, but a few studies show that this doesn’t negatively affect immediate adhesive bonding to instrumented enamel.

Figure 7—SEM micrograph showing the enamel etching pattern after a 15% phosphoric acid etch applied for 15 seconds. Final magnification 3000x.

However, other research shows a significant decrease of the bond strengths. Because of the lack of long-term clinical evidence on the durability of bonding to enamel using these less aggressive conditioners, the previous use of 32% to 40% phosphoric acid conditioner is still the best option to achieve predictable bonding to enamel. However, some authors recommend reducing the etching time to 15 seconds when a 32% to 40% phosphoric acid is used. Most of the manufacturers of adhesive systems have recommended 15 seconds because it is saves time without compromising the adhesive performance.

Reducing times has been suggested because it presents 3 advantages. First, because acid conditioning causes superficial tissue loss, it is desirable that minimal tooth structure be dissolved; therefore, minimal acid-application time should be used. The difference between 15-second and 30-second application time of phosphoric acid on enamel dissolution is very small. The chemical reaction of the conditioning occurs quickly and, as mineral components are lost, the acid potential decreases by buffering. Second, when one is dealing with cavities involving enamel and dentin, the expansion of the etching technique to dentin (also called total-etch technique) is controversial because the time should not be longer than 15 seconds in dentin, but this is the minimum time required to achieve a suitable bonding to enamel. As a result, it has been suggested that the conditioning time be reduced to 15 seconds, which is considered adequate for creating a retentive enamel surface with no difference in the enamel etching pattern or decrease of the bond strengths to instrumented enamel. In vitro studies have demonstrated that a 15-second conditioning time is also adequate for orthodontic adhesive procedures. The third advantage is saving chair time.

A 15-second etching time is sufficient when using 32% to 40% phosphoric acid to achieve a proper bond strength when it is applied to instrumented enamel surfaces or when a cavity preparation has been accomplished. However, in the presence of intact enamel, a different approach may be preferred, which will be discussed later in the article.

Type of Enamel

An important clinical factor in bonding to enamel is the tissue to be bonded. The surface instrumentation, the patient’s age, and environmental factors can lead to subtle differences in enamel characteristics and influence the ability of an acid conditioner to properly demineralize. Several materials have been analyzed in studies on instrumented enamel surfaces. However, it should be taken into account that restorations are commonly extended beyond the margins of the cavity preparation. Also, a number of conservative restorative treatments (eg, diasthema closure, tooth recontouring, restoration of fractured teeth, pit-and-fissure sealing, and bonding of orthodontic devices) are all performed without tissue instrumentation. Because of higher inorganic content, the intact enamel surface presents some unique features. First, young patients’ teeth have an aprismatic layer of approximately 30 µm that covers the entire crown. This layer is lost with time; however, the hard tissue of the teeth becomes more mineralized when exposed to the oral environment in patients with equilibri-
um in the demineralization process. This causes the surface layer of enamel to present hypermineralization features when compared with the innermost enamel.46 These 2 differences can influence the feature of the etching pattern and result in less homogeneous etching patterns,46 compromising the quality of bonding. Figure 8 shows cervical enamel before and after etching with 35% phosphoric acid b for 15 seconds.

The instrumentation of the tissue by a cavity preparation, microetching, or placement of a bevel can change the response of the tissue to the acid etching. Several studies report that the removal of the surface layer of enamel enhances the etching result, and consequently, the bond strength.37,48 A recent study showed that optimal bond strength to aprismatic enamel is achieved by increasing the time of acid etching suggested by the manufacturer from 15 seconds to 30 seconds (with 35% phosphoric acid b).49 It is the authors’ belief that the chemical and morphological characteristics of intact enamel would influence this difference. Further studies must be performed to identify the response of enamel with different mineral features when acid etched.

Cleaning Enamel

Cleaning enamel is an important aspect to consider in bonding to enamel. Some advantages clinicians attribute to acid etching are bactericidal action and cleansing potential. Phosphoric acid has an antibacterial effect.30 To potentiate this effect, some acid conditioners with antibacterial agents (eg, 3% cetypyridinium chloride) have been made available. Without questioning the confidence of this fact, this is not the objective of the acid etching when taking into consideration exclusively bonding to enamel. For a proper etching, the surface of enamel must be clean. This cleaning must be accomplished before etching using cotton pellets soaked in agents such as chlorhexidine gluconate and benzalkonium chloride. Alternatively, the air/water spray of a triple syringe is an option in easy access locations. When the clinician prefers to perform the cleaning after the acid etching, chlorhexidine gluconate (Consepsis Scrub®) and benzalkonium chloride (Tubulicid®) solutions should be preferred to disinfection pastes, because they do not influence the marginal seal.31 Floss and gauze are recommended for proximal surfaces. Prophylactic pastes and Robinson brushes are useful on noninstrumented enamel surfaces. A suitable alternative is a bicarbonate jet.

Bonding to Contaminated Enamel

It has been established that a main reason for debonding is the contamination of the conditioned enamel surface before the application of the adhesive.37 Thus, it is important to control the oral fluids throughout the adhesive procedures to avoid possible contamination of the operative field. Moisture or contamination with oral fluids impairs bonding of resins to enamel32-62 because the etched enamel surface is chemically and physically modified.37,56,63

Because rubber dam isolation is impractical in some instances, there is a risk of surface contamination from blood or saliva and difficulty keeping the surfaces completely dry. This difficulty can be observed in the surgical bonding of traction devices to unerupted teeth,64 or sealing of occlusal surfaces in erupting teeth. These situations are critical because bonding failure requires a new surgical intervention or allows for early marginal microleakage, respectively.

To achieve suitable clinical results, most of the adhesive systems require a contamination-free surface.35-67 There are reports that the bond strength is reduced to 50% when the adhesive is applied directly to contaminated enamel compared with uncontaminated surfaces.60,61,66 To overcome contamination, some manufacturers have introduced hydrophilic adhesives, suggesting their potential to successfully bond to a contaminated enamel surface. The difficulty of bonding to contaminated enamel can be minimized if the adhesive is hydrophilic and has the potential to polymerize completely, even in the presence of moisture.18,19,23,68-70 A few studies have shown that adhesive agents containing hydrophilic monomers can overcome the effect of contaminants on bond strength to contaminated enamel.60,71,72

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*a* Ultradent Products Inc, South Jordan, Utah; www.ultradent.com

b* Global Dental Products, North Bellmore, NY; www.gdpdental.com
Durability of Bonding to Enamel

Bonding to enamel is considered a long-lasting procedure. When the durability of the adhesion is simulated in the laboratory under extensive thermocycling (30,000 cycles), the acid-etching technique in enamel allows for the maintenance of a stable bond strength. Theoretically, an extensive thermocycling (30,000 cycles) is comparable (with limitations) to 3 years of clinical function. However, this stability depends on the adhesive system used. Some systems could be less stable because of excessive concentration of solvents, and the presence of hydrophilic monomers that present high wettability potential. Although these monomers allow for immediate high bond strengths, they are more susceptible to hydrolytic degradation with time when compared with hydrophobic monomers. Another significant variable is the mode of application. The active application (eg, scrubbing the primer on conditioned enamel with a disposable applicator) has a negative effect on the bond strength, mainly regarding durability.

Conclusion

Bonding to enamel is a simple procedure in the dental practice; however, some details can influence its durability. High enamel bond strengths are achieved with previous acid etching. This bonding is sufficiently high to compensate for the polymerization shrinkage of composite resins and an effective marginal seal. This is paramount to obtain a suitable clinical performance of composite resin restorations, preventing marginal leakage, and allowing for adequate retention. Knowing the factors that can influence bonding to enamel is essential when selecting the most appropriate materials and techniques for each situation. For example, it was recently observed that when enamel prisms are exposed perpendicularly, the bond strength is reduced to 50% compared with the parallel exposure of the prisms. Therefore, extreme caution is recommended in the gingival margins of Class II restorations, with the smoothing of enamel with manual instruments, rubber dam isolation, application of etchant beyond all margins, and insertion and polymerization of composite resin in small increments. Taking these details into consideration, more predictable restorations will be obtained.

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References
Quiz 1

1. Enamel’s mineral portion is approximately:
   a. 96% of its weight.
   b. 16% of its weight.
   c. 4% of its weight.
   d. 75% of its weight.

2. Chemical treatment by acid etching does which of the following, changing it from a low-reactive surface into a surface that is more susceptible to adhesion?
   a. enhances the topography
   b. lowers the free energy
   c. minimizes the micromechanical interlocking with the enamel
   d. increases its free energy

3. Acid etching removes approximately 10 µm of enamel surface and creates a morphologically porous layer with how much depth?
   a. 0.5 µm to 5 µm
   b. 0.05 µm to 0.5 µm
   c. 5 µm to 50 µm
   d. less than 0.5 µm

4. Most adhesive systems that use the total-etch technique have in their formulation:
   a. water.
   b. acetone.
   c. low-viscosity hydrophilic monomers.
   d. fluoride.

5. In the early 1990s, it was common to find etchants such as:
   a. 10% maleic acid.
   b. 10% citric acid.
   c. 2.5% nitric acid.
   d. all of the above

6. The use of which concentration of phosphoric acid conditioner is still the best option to achieve predictable bonding to enamel?
   a. 32% to 40%
   b. 2.5% to 10%
   c. 85% to 100%
   d. 10% to 15%

7. Cleaning can be accomplished with:
   a. air/water spray.
   b. chlorhexidine gluconate.
   c. benzalkonium chloride.
   d. all of the above

8. There are reports that the bond strength is reduced to _____ when the adhesive is applied directly to contaminated enamel compared with uncontaminated surfaces.
   a. 5%
   b. 90%
   c. 50%
   d. 75%

9. The durability of bonding to enamel depends on:
   a. the adhesive system used.
   b. excessive concentration of solvents.
   c. the mode of application.
   d. all of the above

10. It was recently observed that when enamel prisms are exposed perpendicularly, the bond strength is reduced to:
    a. 50%.
    b. 10%.
    c. 80%.
    d. 75%.

Please see tester form on page 680.