Adhesive resins are designed to provide strong coupling between resin composites and enamel and dentin. The earliest dental adhesives were relatively hydrophobic and were placed directly on enamel and dentin smear layers (Fig. 1A), although the presence of these layers was unknown at that time. Today, we would call that technique, the no-etch bonding technique. The low bond strength produced by these early adhesives was due to the fact that the adhesives could not penetrate the smear layer and they could not form resin tags. When the bonds were stressed to failure, the fractures occurred within the smear layer (Fig. 1B). That is, the apparent bond strength was actually the intrinsic, cohesive strength of the smear layer (ca. 5-10 MPa) rather than the strength of resin dentin bonds. These low strengths were less than the polymerization stresses (ca. 15-17 MPa) that develop during light curing resin composites. This often led to debonding of one or more sides of a restored cavity, causing postoperative sensitivity, marginal staining and secondary caries. If stronger resin-tooth bonds were to be made, the smear layers would have to be removed. Fortunately, smear layers are very acid labile. Buonocore found that acid-etching enamel caused a large increase in resin enamel bond strength (ca. 20-25 MPa). At that time, the presence of the smear layer was not known. However, Buonocore knew that acid etching removed something that interfered with good resin enamel bonds. The success of bonding resins to acid etched enamel is due to the fact that enamel contains little protein and it can be dried without causing any collapse of the roughened surface. When Buonocore et al. tried those same procedures on dentin, they were disappointed to find that the resin dentin bond strengths to acid etched dentin were very low (5-10 MPa), and were about the same as resin dentin bonds made to smear layer covered dentin. They did not know that acid etching dentin transformed the surface of the dentin into a surface that was similar to the enamel surface.
from a hard, mineralized surface to a very soft mineral-free, collagen-rich surface that collapses when air dried (Fig. 2). Although we now know that acid etching removes the smear layer and smear plugs, thereby making the tubules available for resin tag formation, drying the surface collapses the spaghetti-like collagen fibrils (Fig. 2), making resin infiltration difficult. Over the next 20 years, little progress was made in dentin bonding until the early 1980s. Nakabayashi et al. published their classic paper on how resin infiltration of acid-etched dentin completely transforms the surface from a crystalline, acid sensitive, relatively hydrophilic structure, to an organic, acid resistant, relatively hydrophobic layer. They showed that following acid etching and water rinsing, the mineral phase of dentin is removed. All that is left of the original dentin was the collagenous matrix. The solubilized mineral phase was extracted, but was replaced by resin during resin infiltration. The new surface was neither dentin nor resin, but was a hybrid of both. They coined the term “hybrid layer” to identify the newly formed bioengineered structure. The hybrid layer is very strong and tough when properly formed, and affords enormous micromechanical retention for resin composites.

Nakabayashi’s paper provided new insight and a rationale that explained how resin tooth bonding occurred.

At about the same time in Japan, Professor Fusayama advocated etching both enamel and dentin simultaneously (i.e., the total etch concept). This was a very controversial concept in the U.S. and Europe, where acid etching of dentin was thought to produce pulpal death. However, a careful review of that literature indicated that the pulpal reactions that occurred following acid etching were largely due to inadequate sealing of etched cavities, and were the consequence of bacterial leakage. Over the last decade, decreases in etching time and improvements in bonding formulations and techniques have relegated the acid etching controversy to historical reviews.

Because the total etch technique lead to collapse of the demineralized matrix when it was air dried, the use of primer pretreatments was necessary to re-expand the matrix prior to applying the final bonding agent. Bonding became a 3 step process: total etch and rinse (Fig. 3A), priming and evaporation of solvent (Fig. 3B) and application of the adhesive followed by light curing (Fig. 3C). Another major advance in dentin bonding technique that occurred in the early 1990s was the “wet” (or moist) bonding technique developed by Dr. John Kanca. Prior to that technique, clinicians were taught to acid etch, rinse and dry cavity preparations prior to bonding. What was not recognized at that time was that while normal mineralized dentin could be dried without shrinking, acid etched dentin can not be dried without shrinking 65 vol%. This is because the stiffness of mineralized dentin is 19,000 MPa, while the stiffness of acid etched dentin matrix is 1 MPa. It is literally floating in the rinsing water. If that water is evaporated by air drying, the collagen fibril network collapses (Fig. 2) into a relatively impermeable organic film that interferes with resin infiltration. Resin tags could still be formed, and gave some resin retention, but hybridization of the dentin between tubules (i.e. intertubular dentin) could not occur. This left much naked collagen fibrils in the acid etched layer that could slowly hydrolyze and lead to gap formation between resin and dentin. Kanca discovered that if one left some residual water in acid etched dentin, bond strengths could be doubled. Similar observations were made independently in Japan by Sugizaki. Careful scanning electron microscopy by Gwinnett revealed that wet bonding created thicker hybrid layers (i.e. more resin uptake into etched surfaces) than did dry bonding. However, the ability of acetone or ethanol to “chase” water out of the wet collagen fibril meshwork is often incomplete. The water often diffuses into the organic solvents so fast that the monomers can no longer remain dissolved in the solvents. They undergo phase changes (Fig. 4) that can lead to low bond strengths due to the formation of resin globules and poor resin tag formation, often permitting postoperative sensitivity.

Some manufacturers formulated dentin primers in acetone, while others used ethanol or water. More recently, the primer components have been mixed with adhesives in a single bottle to simplify the number of bonding steps. However, a separate acid etching step is still required (Fig. 5A) in these so called “total etch” wet bonding techniques, followed by application of two layers of bonding agent to wet dentin. The first layer serves the same purpose as did the original primer (purple layer, Fig. 5B). It...
removes much of the residual water and begins to infiltrate adhesive monomers into the acid etched dentin. If the acid etched dentin surface is too wet, phase changes can occur (Fig. 4). Generally, when the second layer of bonding agent is applied, the fresh monomers and their solvent, redissolve the resin globules leaving a more homogeneous film (green layer, Fig. 5B). It appears that the degree of surface wetness that is optimal for ideal dentin bonding varies widely among marketed products. There are no simple answers to the question of how much is “too wet” or “too dry”. Thus, total etch products have become known as “technique sensitive” products. When used in the laboratory on flat dentin surfaces, one can obtain a relatively uniform surface “wetness.” Clinically, however, there is a tendency to over dry the pulpal or axial wall of complex cavities and to pool too much water at axial gingival line angles, leaving the dentin surface with very non-uniform degree of wetness and nonuniform resin infiltration. The gingival floor of proximal boxes is often too wet to achieve perfect bonding, leading to microleakage and sensitivity in those areas.

To avoid the problems associated with total etch/wet bonding techniques, several groups began to explore a new approach to dentin bonding in the early 1990s. All adhesive formulations used in total etch bonding systems contain 5-10 wt% acidic monomers along with other mono or dimethacrylates. The pH of these formulations is between 2.5 and 4.5. These pHs are too high to facilitate solubilization of calcium and phosphate ions from the etched smear layer and underlying intact tooth structure. The dried surface is then covered with a relatively hydrophobic adhesive layer that is light cured (Fig. 6C). The photoinitiators and accelerators in the primer ensure that the primer and adhesive cure together into a seamless unit.

This revolutionary, new approach to bonding comes full circle to where dentin bonding began, i.e. at the smear layer. Although the early adhesives were not acidic enough to etch through the smear layer and were too hydrophobic to wet the smear layer well, the new self etching primers can utilize the smear layer as a legitimate bonding substrate.
(Fig. 7). A great advantage is that self-etching primers are designed to be used on dry dentin. Although one should not over-desiccate dentin, the dentin surface can be briefly dried following cavity preparation because the dentin is mineralized. This avoids all issues of how moist or wet the dentin should be prior to bonding. It is far easier to produce uniform dryness than it is uniform wetness. Another advantage of these self-etching primer systems is that they do not etch very far into the dentin beneath smear layers. This avoids removal of smear plugs in the tubules (Fig. 7) and seems to be responsible for the lack of postoperative sensitivity associated with these technique insensitive adhesive systems19. The shallow etch insures good resin infiltration. Even though the hybrid layer is thin, resin dentin bond strengths are very high19.

The first marketed modern self-etching primer (ca. 1989-1991) was Scotch Prep, the primer portion of Scotchbond 2 (3M Dental Products, St. Paul, MN) consisting of 2.5% maleic acid and 55% HEMA in water (pH 2)19. Unfortunately, this self-etching, self priming system had a relatively short shelf life and the acidity of the maleic acid accelerated the breakdown to HEMA. There was no evidence that the double bond in maleic acid ever copolymerized with HEMA. The first contemporary self-etching primer to be marketed was Kuraray’s Clearfil Liner Bond 2, a light cured product introduced in 1992. Its acidic monomer, Phenyl P, did copolymerizer with the other methacrylate comonomers. This was followed by the introduction of Clearfil Liner Bond 2V, a dual cure self-etching primer system. Recent improvement in catalysts and adhesive monomers lead to the introduction of Clearfil SE Bond in 2000. In the future, a new antibacterial self-etching primer system will be introduced, building upon a decade of research and development of self-etching primer systems by Kuraray Co., Ltd.

Self-etching primer systems should not be confused with all in one self etching, self priming, self adhesive systems such as Prompt L Pop (3M ESPE), One Up Bond F (Tokuyama Corp.), Unifil Bond (G C Corp.), etc. These systems are more acidic (pH < 1) than self etching primers, hence they etch more deeply. They are also more hydrophilic, and tend to produce adhesive films that are overly thin (ca. 10-15 mm). Oxygen in air can diffuse into liquid monomers to a depth of 10-15 mm in seconds. When light cured, the free radicals that are generated are consumed by dissolved oxygen, leading to a lack of polymerization of the monomers even after light curing. When composite filling materials are placed on these unpolymerized resins, they inadvertently displace the adhesive monomers laterally, leaving resin composites in direct contact with hybrid layers. It is desirable to have a thicker (ca. 50 mm) layer of cured adhesive resin between resin composites and hybrid layers to avoid the problems associated with thin oxygen inhibited layers and serve as a shock absorber. The second problem with all in one adhesives is that even if they are thick enough to polymerize, their composition is very acidic and very hydrophilic.”
and absorb water, leading to leaching of un polymerized monomers or hydrolytic degradation products through water filled channels called water trees22 (identified with finger pointers in Fig. 8). The presence of water filled voids and channels are disclosed by soaking bonded specimens in silver nitrate solutions. The filler diffuses into the water filled spaces. Once reduced, it forms black silver deposits. These channels pass from the hybrid layers, through the adhesives to the adhesive composites interface. Adhesive systems that form water trees tend to have lower bond strengths to dental hard tissues, and are less durable than self etching primer systems. In contrast, such water absorption does not occur in self etching primer adhesive systems (such as Clearfil SE Bond) because the etched and primed dentin is sealed by a relatively thick, relatively hydrophobic adhesive layer that prevents water sorption.

These recent advances in adhesive dentistry have been exciting. The development of self etching primer adhesive systems has greatly simplified resin bonding. A separate etching step is no longer required. No rinsing step is required. Bonding can be done under relatively dry conditions, avoiding wet bonding variables. These self etching primer adhesives can be used to etch both ground enamel and dentin simultaneously23. They bond equally well to superficial and deep dentin23 and can be used in place of liners and bases in deep cavities24 if they are covered with an intermediary resin composite such as Protect Liner F (Kuraray Co., Ltd.). The use of caries disclosing agents has no effect on their bond strength25. These self etching primer adhesive systems are so simple to use that they are regarded as "technique insensitive".

Until the all in one adhesive systems are improved, it seems prudent to use self etching primer adhesive systems. The self etching primers have been in widespread use for over 10 years26, whereas the all in one adhesives have only been available for 2 years.

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