

牙體復形學 Operative dentistry

Enamel and Dentin Adhesion Adhesion to Dentin

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學習目標

■ 期許同學在瞭解病患的需求及材料的特性後，能依據所學善加利用，做到不僅是幫病患解決病痛的牙醫師，同時也是個讓病患永遠也忘不了的藝術家。

1. 牙齒的生理，解剖形態
2. 齲齒的生理，診斷及治療計劃
3. 窩洞的修形及材料的選擇
4. 窩洞的充填方式及其修飾
5. 美觀性材料的選擇及其運用
6. 變色牙的修飾

參考資料

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2. Fundamental of operative dentistry. A contemporary approach 3rd edition, James B. Summitt.

Summary

Operative dentistry is the basic science in clinical dental practices. It included dental physiology, morphology, cariology, tooth preparation for restoration. The purpose of Operative dentistry is to complete the function and create the aesthetic outlook.

Successful bonding to enamel was achieved with relative ease, but the development of predictable bonding to dentin has been more problematic. Only recently have dentin adhesive systems produced laboratory results that approach those of enamel bonding, and achieve a predictable level of clinical success.

The chronologic method of classifying dentin bonding systems, the "generational" classification system, is described below. A classification system based on bonding mechanism is described later in the chapter.

Development of Resin Dentin Adhesives First-Generation Adhesives

Imitating his enamel acid-etching technique, Buonocore et al in 1956 reported that glycerophosphoric acid dimethacrylate (GPDM) (see Fig 8-21) could bond to hydrochloric acid-etched dentinal surfaces. The bond strengths attained with this primitive adhesive technique were only 2 to 3 MPa, however, in contrast to the 15 to 20 MPa bond strengths obtained to acid-etched enamel, and the bond was unstable in water) Predating the experiments of Buonocore, other investigators used the same monomer, GPDM, in the early 1950s with the introduction of Sevricon Cavity Seal (Amalgamated Dental Company), an acrylic resin material that could be catalytically polymerized by the action of sulfonic acid.

The development of N-phenylglycine glycidyl methacrylate (NPG-GMA) (see Fig 8-21) was the basis of the first commercially available dentin bonding agent, Cervident (SS White). This first-generation dentin bonding agent theoretically bonded to enamel and dentin by chelation with calcium on the tooth surface and had improved water resistance.

Second-Generation Adhesives

Clearfil Bond System F (Kuraray), introduced in 1978, was the first product of a large second generation of dentin adhesives, such as Bondlite (Kerr/Sybron), J&J VLC Dentin Bonding Agent (Johnson & Johnson Dental), and Scotchbond (3M), among others. These products were based on phosphorous esters of methacrylate derivatives. Their adhesive mechanism involved enhanced surface wetting as well as ionic interaction between negatively charged phosphate groups and positively charged calcium. Although diverse chemical interactions were postulated with either the inorganic or the organic part of dentin (Fig 8-25 and Table 8-2), and are theoretically possible, primary chemical adhesion is not thought to play a major role in the bonding process.

The second-generation systems had modest bond strengths, seldom exceeding 5 to 6 MPa. In those instances in which higher bond strengths were measured, other bonding mechanisms that were unknown at that time were probably involved. Clinical trials of these dentin bonding agents commonly met with poor results. It was speculated that clinical failure was due to inadequate hydrolytic stability in the oral environment, and because their primary bonding was to the smear layer rather than to the underlying dentin. The presence of an intermediate smear layer prevents intimate resin-dentin contact, which is a prerequisite for a chemical reaction.

Third-Generation Adhesives

The basis for the third generation of dentin adhesives was laid when the Japanese philosophy of etching dentin to remove the smear layer gained acceptance. This dentin-acid-etching technique was discouraged in America and Europe until the end of the 1980s because of concerns that acid etchants would induce pulpal inflammation. The postulated bonding mechanism of the dentin-etching technique was that etched dentin would provide micromechanical retention for the restorative resin composite by allowing penetration of the resin bonding agent into the opened dentinal tubules. However, the counterpressure of dentinal fluid and its abundant presence on the bonding site hindered the micromechanical attachment of the early hydrophobic resins. Based on this total-etch concept, Clearfil New Bond was introduced in 1984. It contained HEMA and 10-methacryloyloxy decyl dihydrogen-phosphate (10-MDP) (see Fig 8-21), which had long hydrophobic and short hydrophilic components as active components.

Extensive research in Japan has demonstrated a favorable effect of 4-META (see Fig 8-21) on bonding to dentin. 4-META contains both hydrophobic and hydrophilic chemical groups. In 1982, Nakabayashi et al used this system to describe the micromechanical bonding mechanism that is used by current adhesive systems. With this system, dentin is etched with an aqueous solution of 10% citric acid and 3% ferric chloride, followed by the application of an aqueous solution of 35% HEMA and a self-curing adhesive resin containing 4-META, methyl methacrylate (MMA), and TBB, the last as a polymerization initiator (see Fig 8-21). Based on this technology, adhesive systems such as C&B Metabond (Sun Medical), Super-Bond D-Liner, and Amalgam-bond Plus (Parkell) are commercially available and have been reported to yield consistent results in *in vitro* experiments, regardless of dentinal Depth. (Table 8-3).

Removal of the smear layer with chelating agents such as EDTA was introduced with Gluma. However, irrespective of the use of EDTA, the effectiveness of this system, as mentioned, may have been impaired by the manufacturer's instructions to place the restorative resin, composite over an uncured adhesive resin. Denthesive (Heraeus-Kulzer) also used EDTA to pretreat dentin prior to bonding.

Fourth-Generation Adhesives

Significant advances in adhesive dentistry were made with the development of the multistep dentin adhesive systems in the early-to-mid 1990s. Essential to the enhanced adhesive capacity and responsible for the improved clinical effectiveness of fourth-generation adhesive systems, still in wide use today, is the pretreatment of dentin with conditioners and/or primers that make the heterogeneous and hydrophilic dentin substrate more receptive to bonding. A final step in this relatively complex bonding technique involves the application of a low-viscosity adhesive resin, unfilled or semifilled, that copolymerizes with the primed dentinal surface layer and simultaneously offers bonding receptors for copolymerization with the restorative resin composite. With the multistep application procedure for the fourth-generation adhesives, the term bonding agent was replaced by the term adhesive system.

Fifth-Generation Adhesives

Because of the complexity and number of steps or compounds involved with the fourth-generation systems, researchers and manufacturers have worked to develop simpler adhesive systems. The objective has been to achieve similar or improved bonding and sealing to that provided by the fourth-generation materials, but to do it with fewer "bottles" and/or in less time. Although most of the fifth-generation systems have fallen somewhat short of this objective, the bond strengths achieved by some systems have been comparable to those of fourth-generation systems. Clinical testing and improvement of these systems continue. See the "Adhesive Strategies" section (page 207) for discussion and reclassification of the adhesive systems in use today, commonly called fourth- and fifth-generation systems.

Conditioning of Dentin

Conditioning of dentin can be defined as any chemical alteration of the dentinal surface by acids (or, previously, by the calcium chelator EDTA) with the objective of removing the smear layer and simultaneously demineralizing the dentinal surface. The use of the term conditioner found its origin in the early 1990s when the application of acid etchants to dentin, in particular in the United States and Europe, was taboo because of its alleged harmful effects on the underlying pulp. Conditioners are most commonly used as the initial step in the clinical application of total-etch systems and are therefore applied simultaneously to enamel and dentin following the so-called total-etch technique. Various acids, in varying concentrations, such as citric, maleic, nitric, and phosphoric acids, are supplied with various adhesive systems (see Fig 8-24). After clinical application, these conditioners are generally rinsed off to remove any acid remnants and dissolved calcium phosphates. The only exception was the nitric acid included in ABC Enhanced (Chameleon); the excess etchant was blown off without rinsing. However, this procedure was found to be unfavorable for subsequent resin infiltration.

In addition to removing the smear layer, this superficial demineralization process exposes a microporous scaffold of collagen fibrils (Figs 8-26 to 8-29), thus increasing the microporosity of intertubular dentin. Because this collagen matrix is normally supported by the inorganic dentinal fraction, demineralization causes it to collapse (Fig 8-30). On intertubular dentin, the exposed collagen fibrils are randomly oriented and are often covered by an amorphous phase with relatively few microporosities and of variable thickness (Figs 8-30 and 8-31). The formation of a relatively impermeable amorphous gel on top of the exposed collagen scaffold has been ascribed to the combined effect of denaturation and collapse of residual smear layer collagen. Etchants thickened with silica leave residual silica particles deposited on the surface, but the silica does not appear to plug the intertubular microporosities (Fig 8-27). Sometimes fibrous structures, probably remnants of odontoblastic processes, are pulled out of the tubules and smeared over the surface (Fig 8-32).

The depth of demineralization of the dentinal surface depends on several factors, such as the kind of acid and its application time, the acid concentration and pH, and the other components of the etchant such as surfactants, thickeners (silica vs polymer), and modifiers (Table 8-4). Parameters such as osmolality and viscosity may also be involved in the aggressiveness of demineralization.^{22s,234} The depth of demineralization also appears to be dependent on the distance between tubules. The closer the tubules, the deeper the demineralization. Because acid etching unplugs the dentinal tubules, acid is able to penetrate the tubule to a certain depth (Figs 8-28 to 8-30).

With increasing aggressiveness of the conditioning agent, a circumferential groove may be formed at the tubule orifice, separating a cuff of mineralized peritubular dentin from the surrounding intertubular dentin (Fig 8-33). Alternatively, the mineralized peritubular dentin may be completely dissolved to form a funnel shape (Fig 8-34). In this case, the underlying collagen network, made up primarily of circular collagen fibrils, is exposed (Figs 8-28 and 8-29). The characteristic collagen banding is most visible in the tubule wall.

This demineralization process also changes the surface-free energy of dentin. The high protein content exposed after conditioning with acidic agents is responsible for the low surface-free energy of etched dentin (44.8 dynes/cm), which differentiates it from etched enamel. Wetting of such a low-energy surface is difficult, and adhesion is hard to achieve if the dentinal surface energy is not increased by the use of surface-active promoting agents, or primers.

The dentinal surface may be alternatively modified by the use of hard tissue lasers or microabrasion. With laser technology, the dentinal surface is modified by microscopic explosions caused by thermal transients, increasing the bondable fraction of inorganic dentin and micromechanical retention (Fig 8-35). Microabrasion is based on the removal of demineralized and discolored tooth tissue and results in the formation of a smear layer. It has been suggested that microabrasion may enhance the bonding capability of smear layer-mediated dentin adhesive systems. More research is needed to investigate the potential of these alternative dentinal surface treatments to enhance bonding. They are not presently considered to be proven tooth surface pretreatments.

Primers

Primers serve as the actual adhesion-promoting agents and contain hydrophilic monomers dissolved in organic solvents, such as acetone or ethanol. Because of their volatile characteristics, these solvents can displace water from the dentinal surface and the moist collagen network, promoting the infiltration of monomers through the nanospaces of the exposed collagen network (Figs 8-26 to 8-29 and 8-36). Effective primers contain monomers with hydrophilic properties that have an affinity for the exposed collagen fibril arrangement and hydrophobic properties for copolymerization with the adhesive resin. The objective of this priming step is to transform the hydrophilic dentin surface into a hydrophobic and spongy state that allows the adhesive resin to wet and penetrate the exposed collagen network efficiently.

HEMA, described as essential to the promotion of adhesion because of its excellent wetting characteristics, is found in the primers of many modern adhesive systems. In addition to HEMA, primers contain other monomers, such as NTG-GMA, PMDM, biphenyl dimethacrylate (BPDM), and dipentaerythritol penta acrylate monophosphate (PENTA) (see Fig 8-21). More recent primers, in All-Bond 2 (Bisco), OptiBond (Kerr), and Clearfil Liner Bond System (Kuraray), also include a chemical or photopolymerization initiator, so that these monomers can be polymerized in situ. More viscous primers, as provided by the so-called one-bottle adhesives, were developed to combine the priming and bonding function to simplify the bonding technique (see Table 8-3).

Primers have also been used to treat and prevent dentinal hypersensitivity. Dentinal hypersensitivity is believed to be caused by pressure gradients of dentinal fluid within patent tubules that communicate with the oral environment. Primers may induce denaturation and precipitation of proteins from the dentinal fluid and, consequently, decrease dentinal permeability and outward flow of pulpal fluid, reducing the clinical symptoms of hypersensitivity.

Adhesive Resin

The adhesive resin, also called bonding agent, is equivalent to the enamel bonding agent and consists primarily of hydrophobic monomers, such as bisGMA and UDMA, and more hydrophilic monomers, such as TEG-DMA as a viscosity regulator and HEMA as a wetting agent (see Fig 8-21). The major role of the adhesive resin is to stabilize the hybrid layer and to form resin extensions into the dentinal tubules, called resin tags (Figs 8-37 and 8-38).

Adhesive resins can be light curing and/or autocuring. Autocuring adhesive resins have the theoretical advantage of initial polymerization at the interface due to the higher temperature produced by body heat, but the disadvantage of slow polymerization. For light-curing bonding agents, it is recommended that the adhesive resin be polymerized before the application of the restorative resin. In this way, the adhesive resin is not displaced, and adequate light intensity is available to sufficiently cure and stabilize the resin-tooth bond to resist the stresses produced by polymerization shrinkage of the resin composite. Because oxygen inhibits resin polymerization, an oxygen-inhibited layer of about 15 μm will always be formed on top of the adhesive resin, even after light curing. This oxygen-inhibited layer offers sufficient double MMA bonds (see Fig 8-21) for copolymerization of the adhesive resin with the restorative resin.

Hybridization

Hybridization, or the formation of a hybrid layer, occurs following an initial demineralization of the dentinal surface with an acidic conditioner, exposing a collagen fibril network with interfibrillar microporosities that subsequently becomes interdiffused with low-viscosity monomers (Figs 8-39 and 8-40). This zone, in which resin of the adhesive system micromechanically interlocks with dentinal collagen, is termed the hybrid layer or hybrid zone.

Fig 8-43 Transmission electron photomicrograph of a demineralized section demonstrating the resin-dentin interface produced by the "one-bottle" adhesive Single Bond (3M), known as Scotchbond 1 in Europe. Typical is the deposition of an electron-dense phase (white stars) on top of the hybrid layer (H) and along the tubule orifice walls, often blocking them. This deposition represents a phase separation of the polyalkenoic acid copolymer (from the other monomers) that reacted with calcium to form a calcium-polycarboxylate salt. Because this phase is rich in carboxylic groups, heavy metals from positive staining (lead citrate and uranyl acetate) are easily picked up, resulting in the heavily stained phase. Fragments of the phase are observed as black globules scattered in the adhesive resin (A). The hybrid layer shows an electron density that gradually becomes less intense toward the lab-demineralized intertubular dentin (I). R = resin tags; bar = 2 μm .

This micromechanical bonding mechanism was first described by Nakabayashi et al in 1982 as the formation of a resin-reinforced zone. It took researchers almost 10 years to accept this theory and to further explore this bonding mechanism.

A number of questions remain as to which parameters are of primary importance to adhesive efficacy. First, little is known about the impact of collagen denaturation on the durability of the bond. In this respect, Nakabayashi warned that denaturation of collagen by aggressive acid conditioning may cause bond failure in the long term. Evidence of such collagen denaturation was recorded by Shimokobe et al, preliminarily, and by Okamoto et al, when 37% and 40% phosphoric acid, respectively, were applied to demineralized dentinal collagen. Eick et al also related the presence of remaining cross banding of collagen fibrils inside the hybrid layer to intact undenatured collagen.

- Absence of collagen banding may, however, also indicate that the fibril structure is in a destabilized state, but not necessarily denatured to gelatin. Another study using atomic force microscopy (AFM) revealed disappearance of the 67-nm banding of collagen after etching and air drying. Although it was explained as evidence of denaturation of collagen, the fact that the effect was reversible with the reappearance of collagen banding after storage in water for 1 day most likely indicates that the disappearance of collagen cross banding may be due to contraction of the collagen fibrils as induced by acid etching and air drying.

Another parameter in question is the formation of a relatively impermeable amorphous gel on top of the exposed collagen scaffold that might prevent resin from fully penetrating the demineralized dentin. This gel was ascribed to the combined effect of denaturation and collapse of residual smear layer collagen. A brief application of a weak sodium hypochlorite solution has been suggested to remove the gel; this has preliminarily been found to have a favorable effect on dentin bond strength. Others have used sodium hypochlorite to completely dissolve and remove the collagen layer to expose the underlying pure mineralized dentin, to which adhesives could then be bonded directly. This procedure adds another step to the already technique-sensitive and time-consuming process. Further research is required to explore the efficacy of this approach.

Concerns have been raised that aggressive etching of dentin may cause demineralization to a depth that might be inaccessible to complete resin impregnation. If this occurred, a collagenous band at the base of the hybrid layer, not impregnated by resin, would dramatically weaken the resin-dentin bond and, consequently, the durability of the bond. Incomplete resin penetration has been described as causing a microporous dentinal zone at the base of the hybrid layer, which is thought to be a pathway for nanoleakage of fluids, causing hydrolysis of collagen and a reduction in the longevity of the bond. Microporosities in the hybrid layer have been demonstrated by transmission electron microscopy for some of the first-generation adhesives, so and imperfect resin penetration has been reported for some modern adhesive systems. Other modern adhesive systems have been reported to have completely sealed interfaces.

Another parameter of primary importance to the strength and durability of the resin-dentin bond is the degree of polymerization conversion of resin that has infiltrated the superficially demineralized zone of dentin. Resin monomers might be able to penetrate the demineralized dentin, but, if inadequate in situ polymerization occurs, the longevity of the resin-dentin bond may be compromised. The degree of polymerization inside the hybrid layer will depend on the mode of polymerization (light-activated, or chemically activated, or both), the site of initial polymerization (interfacial or originating in the adhesive resin), and the degree of in situ available double-carbon bonds. Inadequate in situ polymerization within the hybrid layer may act as a reservoir for monomer release and thus have cytotoxic potential.

Finally, as mentioned, water that is already present in the hybrid layer or introduced when a "wet-bonding" technique is used, and residual amounts of solvents such as ethanol and acetone, if not completely evaporated, may affect resin polymerization inside the hybrid layer or at least occupy space that optimally should have been filled with resin.

All of these concerns in relation to hybridization require consideration and further research, because they will eventually determine the quality of the hybrid layer and consequently the hydrolytic stability of the resin-dentin bond in the oral environment.

Resin Tag Formation

Historically, the contribution of the formation of resin tag to bond strength has been a matter of speculation. Bond strength values drop in deeper dentin where the number and size of dentinal tubules is greater and intertubular dentin occupies less of the total bonding area. This indicates that the presence of intertubular dentin is more important than the development of resin tags in the bonding process.

The increased wetness of tubule-rich dentin would be expected to affect the intimate interaction of the adhesive system with the dentinal surface, but the increased hydrophilicity and improved wettability of modern adhesive systems make their bond strengths less affected by the depth and wetness of dentin. With the newest adhesive systems, resin tags have been observed to be intimately attached to the tubule walls with cores of resin surrounded by hybridized tubule walls (Figs 8-41, 8-42, and 8-44). This phenomenon has been termed tubule wall hybridization. It not only provides a firm attachment of the resin-tag necks to the tubule walls but more importantly guarantees hermetic sealing of the tubules that form the direct connection to the pulp.

Resin infiltrates even lateral tubule branches and hybridizes their walls, forming submicron resin tags that are attached to the walls of the lateral tubule branches (Fig 8-45). A similar attachment of resin tags to the tubule walls through hybridization has been described to occur in vivo. The formation of submicron resin tags in lateral tubule branches has also been elegantly illustrated with the tubule anastomosis concept introduced by Chappell et al-s2 (Fig 8-46). Such resin tags, which appear to adapt intimately to the inner tubule walls, most likely contribute to dentin bonding.3-5 In this respect, 15% of the bond strength to dentin obtained with one specific modern adhesive system was ascribed to resin tag formation.

Adhesion Strategies--A Scientific Classification of Modern Adhesives

The most common classification of adhesives is based on the time of their release on the dental market. Typically, four to five generations are distinguished. However, this classification in generations lacks scientific basis and thus does not allow the adhesives to be categorized on objective criteria. A more logical classification of adhesives would be based on the number of clinical application steps and, more importantly, on their interaction with the dentinal substrate.

Smear Layer-Modifying Adhesives

Dentin adhesives that modify the smear layer are based on the concept that the smear layer provides a natural barrier to the pulp, protecting it against bacterial invasion and limiting the outflow of pulpal fluid that might impair bonding efficiency. Efficient wetting and in situ polymerization of monomers infiltrated into the smear layer are expected to reinforce the bonding of the smear layer to the underlying dentinal surface, forming a micromechanical and perhaps chemical bond to underlying dentin. Clinically, these systems require selective etching of enamel in a separate step (see Table 8-3). Most typical in this group are the primers that are applied before the application of polyacid-modified resin composites, or compomers.

The interaction of these adhesives with dentin is very superficial, with only a limited penetration of resin into the dentinal surface (Fig 8-48). This shallow interaction of the adhesive system with dentin, with our any collagen fibril exposure, confirms the weak acidity of these smear layer-modifying primers. The dentinal tubules commonly remain plugged by smear debris.

Smear Layer-Removing Adhesives

Most of today's adhesive systems opt for a complete removal of the smear layer, using a total-etch concept (see Fig 8-47 and Table 8-3). Their mechanism is principally based on the combined effect of hybridization (Fig 8-49) and formation of resin tags. These systems are, in their original configuration, applied in three consecutive steps and subsequently categorized as three-step smear layer-removing adhesives. Even when applied to sclerotic dentin, the relatively aggressive phosphoric-acid etching procedure results in the formation of a loosely organized hybrid layer (Fig 8-50). (See box, page 210, for the advantages and disadvantages of three-step total-etch systems.)

With the newest generation of one-bottle or single-bottle adhesives (Figs 8- 8-47, 8-51, and 8-52 and Table 8-3), the conventional three-step application procedure of smear layer-removing systems has been reduced to two steps by combining the primer with the adhesive resin in one solution. In conventional three-step systems, the primer should ensure efficient wetting of the exposed collagen fibrils, displace any residual surface moisture, transform a hydrophilic into a hydrophobic tissue state, and sufficiently carry monomers into the interfibrillar channels. The adhesive resin should fill the remaining pores between the collagen fibrils, form resin tags that seal the opened dentinal tubules, initiate and advance the polymerization reaction, stabilize the formed hybrid layer and resin tags, and provide sufficient methacrylate double bonds for copolymerization with the successively applied restorative resin. In simplified one-bottle systems, the functions of the primer and the adhesive resin should be perfectly combined (see box).

Before these two-step (one-bottle adhesive) systems can be accepted as valid replacements of their three-step precursors, the effect of their simplified application procedure on hybridization must be further investigated in laboratory and clinical studies. Perdigio et al concluded from a combined interfacial morphology and bond strength study that the adhesive effectiveness of one-bottle adhesives was unpredictable and highly dependent on the adhesive tested. Labella et al reported from a quantitative marginal analysis study that the adaptation of dentin margins in Class 5 restorations was significantly inferior for the one-bottle adhesive Optibond Solo compared to its three-step precursor Optibond FL. No differences in marginal adaptation were observed, however, for Single Bond as compared to Scotchbond Multi-Purpose.

At the enamel margins, the adaptation did not differ for all four adhesives tested. Blunck and Roulet concluded from their quantitative marginal analysis study that some one-bottle adhesives achieved marginal adaptation comparable to that of multibottle adhesives. However, the results obtained with the one-bottle adhesives appeared less consistent than those recorded for multi-step adhesives. In general, one-bottle adhesives appear to perform as well as three-step adhesives when bonding to enamel, whereas bonding to dentin still appears to require treatment with a separate application of primer and adhesive.

Smear Layer-Dissolving Adhesives

A simplified application procedure is also a feature of the smear layer-dissolving adhesives or "self-etching adhesives" (see Table 8-3), which use slightly acidic primers or so-called self-etching primers (see box for self-etching adhesives). These primers partially demineralize the smear layer and the underlying dentin surface without removing the dissolved smear layer remnants or unplugging the tubule orifices (Fig 8-53). As previously mentioned, this concept of self-etching primers has already been introduced with an earlier generation of Scotchbond 2-like systems, such as ART Bond, Ecusit Primer-Mono (DMG), and Syntac.

However, these systems are advocated for dentin bonding only and, therefore, require selective enamel etching in a separate step. The current two-step smear layer-dissolving adhesives provide self-etching primers for simultaneous conditioning and priming of both enamel and dentin. Simplification of the clinical application procedure is obtained not only by reduction of application steps, but by omission of a post conditioning rinsing phase. In fact, these condi-primers are only air dispersed without rinsing. As a supplementary advantage, the controversy of post-conditioning drying or keeping the dentin moist, as in a wet-bonding technique (described later), is avoided. The actual rationale behind these systems is to superficially demineralize dentin and to simultaneously penetrate it to the depth of demineralization with monomers that can be polymerized in situ (Figs 8-54 and 8-55).

The second group consists of adhesive systems such as Prompt L-Pop (ESPE), a self-etching adhesive, and Prime&Bond NT (Dentsply) in which a nonrinse conditioner (NRC) is used as a self-etching primer treatment (see Table 8-3). These adhesives have a pH of 1 or less and interact more profoundly with dentin. Hybrid layers reach a thickness of 2 to 3 lam and have the typical interfacial characteristics of a loosely organized collagen fibril network with individual fibrils separated by interfibrillar spaces ("shag-carpet" appearance) (Figs 8-57 and 8-58) at the top of the hybrid layer, "tubule wall hybridization," and "lateral tubule hybridization." Despite the fact that these "strong" self-etching primers are not rinsed off, their interracial ultramorphologic features closely resemble those of total-etch systems that use phosphoric acid that is rinsed off.

Glass-Ionomer Adhesives

A totally new evolution in glass-ionomer adhesives was introduced with Fuji Bond LC (GC), an adhesive material based on resin-modified glass-ionomer technology. It is a resin-diluted version of the resin-modified glass-ionomer restorative material Fuji II LC (GC). Because this glass-ionomer-based adhesive system originates from combined glass-ionomer and resin adhesive technology, one can speculate that its mechanism of adhesion may also be based on a combined micromechanical and chemical interaction with the dentinal substrate. A short polyalkenoic acid pretreatment cleans the tooth surface, removes the smear layer, and exposes surface collagen fibrils to a depth of about 0.5 µm.

Glass-Ionomer Adhesives

Resin interdiffuses with the establishment of a micromechanical bond following the principles of hybridization (Fig 8-59). The polyalkenoic acid pretreatment is much less severe than a traditional phosphoric-acid treatment in that the exposed collagen fibrils are not completely denuded of hydroxyapatite (Fig 8-60). Chemical bonding is obtained by ionic interaction of the carboxyl groups of the polyalkenoic acid with calcium of hydroxyapatite that remained attached to the collagen fibrils. This supplementary chemical attachment may be beneficial in terms of sealing (see box).

Critical Steps in Adhesion Isolation

Before any bonding procedure is begun, adequate isolation and moisture control of the substrate to be bonded to must be achieved. Bonding to acid-etched enamel theoretically requires an air-dried surface to allow the photopolymerizable hydrophobic bonding resin to be drawn by capillary attraction into the pits created by acid etching.

With bonding to dentin, a distinction should be made between an internal and external dentinal wetness. Internal dentinal wetness is caused by pulpal fluids that flow from the pulp through the dentinal tubules, if unplugged by acid etching, to exude onto the dentin cavity surface. This internal dentinal wetness and its effects on adhesion to dentin have been thoroughly documented in literature dealing with the aspects of dentin permeability, as published by Pashley and colleagues. In this respect, first-generation adhesive systems were too hydrophobic to sufficiently wet the hydrophilic dentinal substrate that was etched with concentrated phosphoric acid in simulation of the successful enamel acid-etch technique. As knowledge of the heterogeneous and hydrophilic nature of dentin has become more complete, newer adhesive formulations have been developed for enhanced hydrophilicity and improved wettability.

An accidental form of external dentinal wetness is contamination of the substrate with external fluids, impeding effective contact between the adhesive and the bonding substrate. Salivary contamination is detrimental because saliva contains proteins that may block adequate infiltration of resin in the microretentive porosities created on acid-etched enamel and dentin. Because maxillary teeth are more easily isolated, dentin adhesion appears more effective in maxillary than in mandibular teeth⁵⁷ Consistent use of a rubber dam remains the most effective method of moisture control.

Dentin and Pulp Protection

Once the teeth in need of adhesive restoration have been adequately isolated, a decision must be made about the need for any kind of dentin protection. The use of "nonadhesive" liners and bases beneath adhesive restorations is not recommended. Adhesive materials such as glass-ionomer cements can be used ("sandwich" restoration), but in most cases the simple application of an appropriate adhesive is effective. As mentioned, studies using microscopic examination have demonstrated that adhesives can hermetically seal tubules through tubule wall hybridization (see Figs 8-41a, 8-44, 8-50, 8-52, and 8-58b).

Universal Enamel-Dentin Conditioning Phosphoric Acid Alternatives

After the tooth in need of an adhesive restoration has been adequately isolated and cleaned, a proper etching or conditioning agent must be selected. As mentioned, in most modern adhesive systems, the selective enamel-etching technique used by older-generation bonding agents is replaced in smear layer-removing systems by a total-etch concept, in which the conditioner or acid etchant is applied simultaneously to enamel and dentin. As a result, two different microretentive surfaces are exposed in which the adhesive resin will become micromechanically interlocked. Although most research dealing with adhesive techniques has focused on producing good and stable bonds to dentin, the importance of enamel bonding cannot be neglected with the development of new adhesive systems.

Traditionally, enamel was selectively etched with phosphoric acid in a concentration between 30% and 40%. With the introduction of the total-etch technique, less concentrated phosphoric acids or weaker acids in varying concentrations, such as citric, maleic, nitric, and oxalic acid, have been supplied with various adhesive systems (see Fig 8-24). The objective of such universal enamel-dentin conditioning agents is to find the best compromise between etching enamel sufficiently to create a microretentive etch pattern and etching dentin mildly, avoiding exposure of collagen to a depth that is inaccessible for complete infiltration by resin.³²⁶ However, a few years after the introduction of alternative total etchants into clinical practice, a steadily growing number of clinical trials, as well as laboratory studies,^{298,3-9} demonstrated a less consistent and inferior enamel bond with the use of these less aggressive alternative etchants.

Two different etchants specifically adapted for enamel and dentin could be used, but this is clinically impractical. Using only a weak acid is acceptable if the enamel surface is mechanically roughened before etching or if the acid gel is rubbed vigorously on the enamel surface. Today, most adhesive systems again use conventional phosphoric acid etchants in concentrations above 30% to etch both enamel and dentin in one application. It is recommended that these etchants be applied first to enamel, so that enamel is etched for at least 15 seconds. Only sclerotic dentin surfaces can be etched longer without the risk of etching too deeply. In fact, this hypermineralized tissue should be etched longer to make it more receptive to bonding.

In all smear layer-removing systems, the conditioner and its by-products should be thoroughly rinsed away before application of the primer and the adhesive resin. For example, failure to rinse off the nitric acid conditioner, as recommended by the manufacturer of ABC Enhanced (Chameleon), resulted in an incomplete resin penetration of the demineralized dentin surface layer and minimal hybrid layer formation. Properly rinsed, the conditioner was sufficient to achieve adequate hybridization.

Self-Etch Approach on Enamel

Another recent innovation in bonding to enamel is the use of self-etching primers on both enamel and dentin as part of one- and two-step smear layer-dissolving systems (Fig 8-61 and Table 8-3). Self-etching primers containing acidic monomers, like phenyl-P,³⁴² are air dispersed and not rinsed off, simplifying the application procedure. However, major controversy exists about the etching efficiency of these self-etching primers and the resultant enamel bond strength and stability. PerdigSo et al recently concluded, from a combined enamel shear bond strength and SEM study, that although the phenyl-P self-etching primer did not etch enamel as deeply as conventional etchants, Clearfil Liner Bond 2 demonstrated good bond strengths to enamel.

In the measurement of the microtensile bond strength ($\mu\text{TB}\Sigma\sigma$) to enamel with two self-etching adhesives, the relatively severe self-etching NRC/Prime&-Bond NT and even the moderate self-etching Clearfil SE Bond provided bond strengths comparable to those of the conventional three-step total-etch adhesive Optibond FL. It is noteworthy that in this study all adhesives were bonded to enamel, which had been prepared with 600-grit sandpaper leaving a smear layer. Similar results were reported in another study by Kanemura et al, which revealed that two other self-etching adhesives (Clearfil Liner Bond 2; Mac Bond 2, Tokuyama) produced μTBS s to ground enamel that were comparable to those measured for two one-bottle adhesives (One-Step and Single Bond) that involved a separate phosphoric acid treatment. When the self-etching adhesives were directly bonded to unground, intact enamel, the resultant IJTBS values were, however, significantly lower.

Long-term clinical trials are needed to confirm this promising enamel bonding effectiveness recorded in vitro. Until then, it remains clinically advisable to use this simplified application technique only on enamel that has been coarsened by bur. Additionally, the self-etching primer should be applied for at least 30 seconds and actively applied by rubbing the dentin surface with repeated application of fresh material. Alternatively, a separate conventional etchant can be applied before application of the self-etching primer.

Compomers

Modification of the monomer backbone of conventional resin composites by adding acidic carboxylic groups has recently led to a new group of adhesive restorative materials. On the basis of their composition, they should be regarded as polyacid-modified resin composites, but products such as Dyract (Dentsply), Dyract AP (Dentsply), Hytac (ESPE), Luxat (DMG), and F2000 (3M) are commercially advertised as so-called compomers. This term does not encompass the true characteristics of these materials, however, since it suggests that they originate from combined resin composite and glass-ionomer technology. These materials, in fact, behave more like resin composites. The popularity of the compomers among clinicians must be attributed to their superb clinical handling and simple application method, with only a self-etching primer required to pretreat the enamel and dentin surface.

The primers, which usually contain acidic monomers dissolved in acetone, like most one-bottle primer/adhesive combinations, are only mildly acidic. They interact superficially, to a depth of about 200 nm, with dentin (comparable effect as that seen in Fig 8-48) and are not aggressive enough to expose a highly retentive etch pattern on enamel surfaces. Moreover, recent clinical trials reported the occurrence of minimal to severe enamel margin chipping after only 6 months of clinical service, which, if left untreated, could rapidly lead to marginal discoloration and even caries.^{14,15} These early enamel margin defects are due to ineffective etching of enamel using only the mild, self-etching primers. These clinical results were confirmed in vitro, where the primer provided with Dyract produced relatively low bond strengths to enamel. Most likely, the clinical effectiveness of these polyacid-modified composites could be substantially improved by supplementary acid etching of the enamel before primer application.

Wet Vs Dry Bonding

After conditioning, the enamel and dentin surfaces should be properly treated to allow full penetration of adhesive monomers. On the enamel surface, a dry condition is theoretically preferred. On the dentin site, a certain amount of moisture is needed to avoid collapse of the exposed collagen scaffold, which impedes effective penetration of adhesive monomers (Figs 8-62 and 8-63). Consequently, in the treatment of enamel and dentin, it is difficult to achieve the optimal environment for both substrates. One way to achieve this goal is to keep the substrate field dry and to use adhesive systems with water-based primers to rehydrate, and thus re-expand, the collapsed collagen network, enabling the resin monomer to interdiffuse efficiently. The alternative is to keep the acid-etched dentin surface moist and to rely on the water-chasing capacity of acetone-based primers. This clinical technique, commonly referred to as "wet bonding," was introduced by Kanca¹⁵⁴⁻¹⁵⁶ and Gwin-nett in the early 1990s.

It is fundamentally important to effective hybridization that the collagen fibril web, deprived of its mineral support following acid treatment, keeps its spongelike quality, allowing interdiffusion of resin monomers in the subsequent priming and bonding steps. Dehydration of the acid-conditioned dentin surface through air drying is thought to induce surface tension stress, causing the exposed collagen network to collapse, shrink, and form a compact coagulate that is impenetrable to resin. If some water remains inside the interfibrillar spaces, the loose quality of the collagen matrix is maintained and the interfibrillar spaces are left open. An appropriate amount of moisture on the dentin surface has also been reported to promote the polymerization reaction of specific monomers. The wet-bonding technique has repeatedly been reported to increase in vitro bond strengths.

These monomers have hydrophilic ends with an affinity for the exposed collagen fibrils and hydrophobic ends that form receptors for copolymerization with the adhesive resin. When the water inside the collagen network is not completely displaced, the polymerization of resin inside the hybrid layer may be affected or, at least, the remaining water will compete for space with resin inside the demineralized dentin. The risk that all of the moisture on an overwet dentin surface may not be completely replaced by hydrophilic primer monomers has been well documented for adhesive systems that provide water-free acetone-based primers.

In such overwet conditions, excessive water that was incompletely removed during priming appeared to cause phase separation of the hydrophobic and hydrophilic monomer components, resulting in blister and globule formation at the resin-dentin interface. Such interface deficiencies undoubtedly weaken the resin-dentin bond and result in incompletely sealed tubules. On the other hand, even gentle drying of the dentin surface, for times as short as 3 seconds prior to the application of a water-free, acetone-based primer, has been shown to result in incomplete intertubular resin infiltration. Ineffective resin penetration due to collagen collapse has been observed ultramorphologically as the formation of a so-called hybridoid zone (Figs 8-64 and 8-65).

These hybridoid zones inside the hybrid layer do not appear electron dense on demineralized TEM sections. Consequently, this wet-bonding technique appears technique-sensitive, especially in terms of the precise amount of moisture that should be kept on the dentin surface after conditioning. In other words, acid-etched dentin should not be kept too wet but also should not be dried too long. A short air blast or blotting of the excess water with a dry sponge or small piece of tissue paper have been recommended as most effective in wet-bonding procedures.

This wet-bonding technique has two other disadvantages of clinical importance. First, acetone quickly evaporates from the primer bottle so that, after the primer solution is dispensed in a dappen dish, the primer bottle should be immediately closed and the primer solution immediately applied to the etched surface. Despite careful handling, the composition of the primer solution may change after several uses due to rapid evaporation of solvent. This will increase the ratio of monomers to the acetone content and will eventually affect the penetrability of monomers into the exposed collagen network. To reduce the problem of rapid primer solvent volatilization, special delivery systems have been developed.

Examples are the "bubble mixer" syringe system of Permagen (Ultradent), a syringe system with a disposable application brush for Permaquik and PQ1 (Ultradent), or a delivery system with predose, single-use capsules introduced with Optibond Solo, Optibond Solo Plus, and Excite (Vi-vadent). Another disadvantage of keeping the cavity walls wet after conditioning is that one cannot observe the white, frosted appearance of the enamel that indicates that it has been properly etched.

Adhesive systems that provide water-dissolved primers have been demonstrated to bond equally effectively to dry or wet dentin. In one study, the hybridization effectiveness of two three-step smear layer-removing adhesive systems, Optibond Dual Cure and Scotchbond Multi-Purpose, were examined by TEM. No substantial difference in the ultrastructure conditioning for about 5 seconds, or until the glossy wet surface turns dull and the acid-etched enamel surface appears white and frosted. Future research should clarify and further define this self-rewetting effect in other adhesive systems that include water-based primers.

Primer Application

Primers should clinically be applied with care to ensure that resin effectively infiltrates the network of interfibrillar collagen channels. A primer application time of at least 15 seconds, as recommended by most manufacturers, should be respected to allow monomers to interdiffuse to the complete depth of surface demineralization. When a dry-bonding technique is followed with self-rewetting water-based primers, this 15-second primer application time should allow the gently air-dried and thus collapsed collagen scaffold to re-expand. With a wet-bonding technique, the primer should be applied for at least 15 seconds to displace all remaining surface moisture through concurrent evaporation of the primer solvent carrier. Moreover, water-free, acetone-based primers, provided with three- and two-step (single-bottle) smear layer-removing adhesive systems, should be applied copiously in multiple layers. After brief, gentle air drying, the primed surface should appear glossy.

The primer should be actively rubbed into the dentin surface with disposable brushes or sponge applicators. This may improve and accelerate the monomer interdiffusion process. The typical "shag carpet" appearance of collagen fibrils, which are directed up toward the adhesive resin and appear to be frayed into their microfibrils (Figs 8-41b, 8-50, 8-55, and 8-66), has been attributed to this active rubbing application method). A similar pattern of deeply tufted collagen fibrils has been observed to result from citric-acid burnishing of a root surface as part of a tissue regenerative periodontal treatment.

The physical rubbing action, combined with the chemical action of citric acid, was found to enhance the removal of chemically dissolved inorganic dentin material and surface debris, exposing a deeply tufted collagen fibril surface topography. Likewise, the combined mechanical/chemical action of rubbing the dentin surface with a slightly acidic primer probably dissolves additional inorganic dentin material, while fluffing and separating the entangled dentin collagen at the surface.

Acid-etched enamel does not need a separate primer application to achieve effective bonding when an unfilled or low-filled hydrophobic enamel bonding agent is applied on air-dried enamel. On the other hand, primers can be applied on acid-etched enamel without harming the enamel bonding process. In the wet-bonding technique, primers should always be applied on acid-etched enamel to displace any residual surface moisture through concurrent evaporation of the primer's solvent carrier. The primer application should be completed by short and gentle air drying to volatilize any remaining solvent excess before application of the adhesive resin.

Adhesive Resin Application

In the final step of the bonding process, the adhesive layer is placed. Spreading of the adhesive resin over the surface to be bonded should be done by brush thinning rather than by air thinning. The adhesive should be placed and then evenly spread with a brush tip that can be blotted repeatedly with a paper tissue. In this way, the adhesive resin layer will reach an optimal thickness of about 100 μm . When placed in a sufficiently thick layer, the adhesive resin may act as a stress-relaxation buffer (see Fig 8-19) and absorb some of the tensile stresses imposed by polymerization contraction of the resin composite placed over the adhesive resin. Thinning the adhesive resin layer with an air syringe may reduce its thickness too much, decreasing its elastic buffer potential.

In support of this elastic bonding concept, dentin adhesive systems that provide a low-viscosity resin have been reported to produce higher bond strengths and less microleakage. Microleakage was also found to be reduced when a filled low-viscosity resin was used as an intermediate liner. This elastic bonding concept can be regarded as an efficient means not only to counteract the polymerization contraction stress of the resin composite, but to aid in absorbing masticatory forces, tooth flexure effects, and thermal cycling shocks, all of which may jeopardize the integrity of the resin-tooth bond.

This innovative concept for relaxation of polymerization shrinkage by elastic compensation was adopted by several modern adhesive systems. Clearfil Liner Bond systems 1 and 2 provide a low-viscosity resin, filled with silanated microfiller and prepolymerized filler at 42 wt%. Optibond DC, Optibond FL, Optibond Solo, and Optibond Solo Plus provide a light-polymerizable adhesive resin that contains radiopaque, fluoride-releasing glass filler particles at 48 wt% (see Figs 8-38, 8-41, 8-49, 8-50, and 8-52). A filled adhesive resin is also supplied with other modern adhesives (see Table 8-3). In addition to alleviating stress, these semifilled adhesive resins undergo less polymerization contraction.

They have superior physical properties, with a compressive strength approximating that of microfilled resin composites, and a Young's modulus of elasticity closer to that of resin composites. They form particle-reinforced resin tags as anchors in the dentinal tubules (see Figs 8-38, 8-41, 8-50, and 8-52). Some may release fluoride to the surrounding demineralized dentin and may provide improved esthetics by preventing the formation of a prism effect or a translucent line around the restoration's margins.

Apart from adhesives that provide low-viscosity particle-filled resins (see Table 8-3), thick adhesive layers are also placed with polyalkenoic acid-based adhesive systems, such as Scotchbond Multi-Purpose and Single Bond, and with the more recently developed glass-ionomer-based adhesive system, Fuji Bond LC. Excellent clinical results have been reported for Clearfil Liner Bond, Scotchbond Multi-Purpose, and Optibond Dual Cure in clinical trials.

For light-cured bonding agents, the adhesive resin should always be cured before the application of the restorative resin composite. In this way, the adhesive resin is not displaced when the restorative resin composite is applied, and adequate light intensity is provided to sufficiently cure the adhesive resin layer. Curing the adhesive resin prior to inserting resin composite will stabilize the resin-tooth bond and consequently activate the elastic stress-relaxation mechanism.

Because of oxygen inhibition, the top 15 μm of the adhesive resin will not polymerize, but will provide sufficient double methacrylate bonds for copolymerization with the restorative resin. Again, brush thinning rather than air thinning may prevent the film thickness from being reduced to an extent that the air-inhibited layer permeates the whole resin layer, reducing the stress-relaxation capacity and bond effectiveness.

Restorative Procedure

As long as resin composites shrink during polymerization, additional clinical measures will be needed to compensate for the polymerization shrinkage. In addition to building in a flexible stress-absorbing bonding interface, the restorative material should be placed in such a manner that the polymerization contraction stress is clinically reduced as much as possible. An in vivo study by Perdigão showed that, in bulk-filled Class 1 cavities, the dentin-adhesive was not able to withstand polymerization shrinkage stress. Almost consistent detachment of the adhesive resin from the underlying hybrid layer was observed. In that study, porosities incorporated in relatively thick adhesive resin layers were found to result in less frequent resin-dentin interface separation, providing support for the elastic bonding concept. These observations also confirm the influence of the cavity geometry or configuration on the eventual bond integrity, with Class 1 cavities having the most unfavorable geometry, as previously described. (see Fig 8-18).

Amalgam Bonding

The use of adhesive technology to bond amalgam to tooth tissue is an application of universal or multipurpose adhesive systems. Adhesive systems such as All-Bond 2 (Bisco), Amalgambond Plus (Parkell), Panavia (Kuraray), and Scotchbond Multi-Purpose Plus have been advocated for bonding amalgam to enamel and dentin. The nature of the bond between resin and amalgam is yet unclear, but appears to involve at least micromechanical mixing of amalgam with resin during condensation (Fig 8-67). Because amalgam does not allow light transmission, these amalgam-bonding systems must have autopolymerizing capability. In vitro bond strengths of amalgam to dentin are generally less than 10 MPa, which is less than bond strengths of resin composite to dentin. A possible problem with the incorporation of resin into amalgam is potential weakening of the mechanical properties of the bonded amalgam.

The use of amalgam-bonding techniques has several potential benefits. Retention gained by bonding lessens the need for removal of tooth structure to gain retention or for retentive devices such as dovetails, grooves, and parapulpal pins. Bonded amalgam may increase the fracture resistance of restored teeth, and adhesive resin liners may seal the margins better than traditional cavity varnishes, with decreased risks for postoperative sensitivity and caries recurrence. Although these amalgam-bonding techniques have been advocated for repair of existing amalgam restorations with either resin or fresh amalgam, several studies have reported poor results in the strengthening of old amalgam restorations.