

Dentine Bonding Systems: I. Mode of Action

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Abstract: The achievement of a reliable bond to dentine has been more difficult than bonding to enamel, due principally to the anatomy of the dentine substrate. The mechanisms of bonding are now much better understood than a decade ago and clinically-viable bond strengths to dentine are now achieved with many dentine bonding systems.

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Clinical Relevance: The improved reliability of current dentine bonding systems has resulted in an expansion of their clinical applications.

The production of a stable, long-term bond to tooth substance is an ideal requirement for the success of all restorations, both metallic and non-metallic. The magnitude of this bond must be sufficient to withstand the stresses caused by the polymerization contraction of resin-based materials, generally considered to be about 17 MPa in low-configuration factor restorations (i.e. those in which the ratio of bonded to non-bonded surfaces is one or less than one),¹ and steps must be taken to prevent these stresses from compromising the restoration.² The strength of the bond should also be enough to retain restorations in non-invasive, non-retentive cavity preparations which may preserve tooth substance and minimize the potential

for pulpal damage during cavity preparation.

HISTORICAL OVERVIEW

First reports in laboratory studies of the achievement of a bond to dentine were the publications in 1952 by Kramer and McLean³ and in 1955 by Buonocore.^{4,5} The adhesive used by Kramer and McLean was not disclosed but they speculated that it might contain methacrylic acid, which could result in the stain-altered dentine these workers observed. The adhesive described by Buonocore was essentially a dimethacrylate with appended phosphate groups: these groups used the potential for chemical bonding by ionic bonds to the calcium in the dentine. The bond strengths reported by Buonocore were low (5.7 MPa) and the bonds obtained were not hydrolytically stable, which resulted in a decrease in the bond strength value to 2.7 MPa after five months.⁴ In 1965 Bowen published details of a system which used surface-active *N*-phenyl

glycine glycidyl methacrylate (NPG-GMA) to enhance the wetting of the dentine surface and thereby improve adhesion.⁶

Later systems, termed second-generation systems, changed the calcium-phosphate-resin concept described above by modifying resins such as *bis*-GMA, but these were only slightly more reliable than the earliest systems.

It was not until the mid-1980s that systems were developed which demonstrated any clinical reliability. Most of these 'third-generation' systems used a solution, or series of solutions, to increase the wettability of the dentine surface before application of the resin.⁷ These systems also used more hydrophilic resins, with a number of different resins being used in each system. Another system, GLUMA (Bayer Dental, Leverkusen, Germany), contained 2-hydroxyethyl methacrylate (HEMA) (Figure 1) and glutaraldehyde. Bonding was achieved by a reaction between the glutaraldehyde and amino groups in the collagen to form charged compounds, which in turn reacted with the hydroxyl group of the HEMA molecule, and by a mechanical interlocking in the opened ends of the dentinal tubules.⁸ The use of additional priming solutions in the third-generation systems made their use more time consuming and technique sensitive than previous materials, but the bond strengths to dentine were generally higher and more reliable in the oral environment.⁷ Nevertheless, the bond strengths of these

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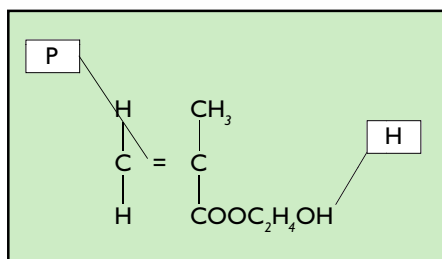


Figure 1. The chemical formula of 2-hydroxyethyl methacrylate (HEMA). H = hydrophilic group; P = double bond capable of polymerization.

systems were generally lower than the value considered sufficient to withstand the stresses generated by the polymerization shrinkage of a resin-composite material (17 MPa, as mentioned above). Third-generation dentine bonding agents were generally considered to achieve bonding to dentine by penetration of the smear layer—i.e. they used micromechanical means of adhesion rather than the unreliable chemical bonding of previous materials.

‘Fourth-generation’ dentine bonding systems used a different concept to that of the third generation. In these systems, the smear layer was removed with a chemical conditioner and the resin(s) bonded to dentine using micromechanical retention by way of a ‘hybrid layer’ in which the decalcified uppermost 5 to 10 mm of dentine is penetrated by resin. This hybrid layer was first recognized by Nakabayashi and was considered to be a combination of resin and tooth.⁹ Some retention may also be achieved by tubular penetration (Figure 2).

‘Fifth-generation’ materials are now available; these are similar in principle to the fourth-generation materials, except that they have been designed to require fewer stages in their placement, in an attempt to reduce technique sensitivity and treatment time. However, not all of the so-called fifth-generation systems are faster in clinical use than their fourth-generation predecessors.

DIFFICULTIES IN BONDING TO DENTINE

The ability to form a bond between a resin-based material and acid-etched

enamel was first demonstrated by Buonocore in 1955,⁴ but the clinical technique of bonding to enamel did not become established until the early 1970s—possibly because of the unavailability of a suitable restorative material until that time. Bonding to dentine has proved to be more problematic for a number of reasons. Among these are:

- Dentine contains up to 22% water by volume (Table 1),¹⁰ and many resins are hydrophobic.
- Within the dentine there are many variations in substrate: for example, Pashley has calculated that only 1% of the dentine surface close to the enamel is composed of fluid-filled tubules, while 1 mm from the pulp 22% of the dentine surface is made up of tubules.¹¹ Furthermore, sclerosed dentine presents greater problems in bonding due to the difficulties of penetrating the sclerosed surface. In this respect, it has been suggested that the removal of a small amount of the shiny, sclerotic dentine may facilitate resin penetration.¹²
- A ‘smear layer’ composed of debris and demineralized subsurface dentine is present on a cut dentine surface, and it is now considered that this layer is of limited strength, so it must either be removed before application of a bonding resin or penetrated by the resin.¹³ As smear layer removing systems have been shown to perform better clinically than smear layer modifying systems, the removal of the smear layer appears to be indicated.¹⁴ Furthermore, because the smear layer contains bacteria, it should be removed by an appropriate



Figure 2. Diagrammatic representation of the hybrid layer. A collagen mesh, present on the dentine surface after decalcification (top diagram), is infiltrated by resin (blue dots, middle diagram). If the decalcified surface is allowed to dry out, the collagen layer shrinks and cannot be penetrated by resin (bottom diagram).

chemical before placement of the restoration.

- As outlined above, the bond to dentine must be greater than the stresses caused by polymerization shrinkage of the resin restoration placed against it. It must also resist the stresses generated by finishing and polishing the restoration shortly after placement and the stresses from occlusal forces on the completed restoration.
- If the smear layer and smear plugs (see below) are removed by an application of acid, the dentine surface will be moist due to tubule fluid outflow. A dentine bonding system must therefore be able to operate satisfactorily on such a moist surface.
- A dentine bonding system must be biocompatible.

THE IDEAL DENTINE BONDING SYSTEM

Ideally, a dentine bonding system should:¹⁵

	Enamel		Dentine	
	Weight	Volume	Weight	Volume
Mineral	97	92	70	45
Organic	1	2	20	33
Water	2	6	10	22

Table 1. Percentage composition of enamel and dentine.¹⁰

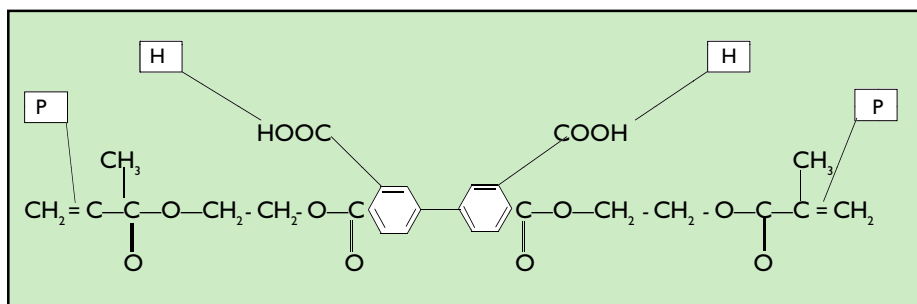


Figure 3. A biphenyl dimethacrylate (BPDM) molecule with hydrophilic carboxylate groups (H) and polymerizable methacrylate groups (P).

- provide an immediate, permanent, high-strength bond to dentine;
- have a bond strength to dentine similar to that to enamel;
- be compatible with dental tissues;
- minimize microleakage at the margins of restorations;
- prevent recurrent caries and marginal staining;
- be easy to use and minimally technique sensitive;
- have a reasonable shelf life;
- be compatible with a wide range of resins;
- use a resin of low film thickness (> 20µm) if the system is to be suitable for use with indirect restorations
- show no reduction in bond strength when applied to a moist surface; and
- have no potential for sensitization of patients or operators.

The bond strength to dentine should be equal to or greater than the bond to enamel and should mature rapidly—ideally within 5 minutes. A bond strength to dentine at least equal to that to enamel is necessary because debonding of the system may occur at the dentine surface if the bond to dentine is less than to enamel, with the restoration remaining adherent to enamel and bringing the potential for leakage, sensitivity and ultimately secondary caries.

CURRENT DENTINE BONDING SYSTEMS

Currently available dentine bonding systems generally comprise an etchant

or conditioner and/or primer and a bonding resin.

Etchant

Etching of dentine was met initially with suspicion by many dental practitioners. Indeed, such practice was considered in 1978 to promote an undesirable pulpal response that was exacerbated by the subsequent placement of restorative resin.¹⁶

However, Fusayama used a system which involved the etching of dentine with success, stating 'total etching including both enamel and dentine ... does not promote pulp irritation, but rather decreases it instead.'¹⁷ More recently, Kanca has suggested that early work which demonstrated that etching was detrimental to pulpal tissue reached an incorrect conclusion in that the pulpal inflammation that was noted following application of acids to

dentine was a result of poor sealing of the cavity (and the dentine surface) and the potential for eugenol to be an irritant.¹⁸ It is therefore essential that the etched dentine surface is adequately 'sealed' by the bonding resin.

Brannstrom considers that sealing of the dentine surface prevents the formation of any space between restoration and tooth, and that it is bacterial invasion of the space formed by a defective bond that leads to pulpal irritation, which the patient experiences as sensitivity.¹⁹

The acid etchant or conditioner acts by removing the smear layer and opening the dentinal tubules by removing the smear plugs. It decalcifies the uppermost 10 to 15 µm of the intertubular and peritubular dentine. Currently, most systems use 35% phosphoric acid, although 15-25% phosphoric acid, 3% nitric acid or 10% maleic acid are used in some systems. Some systems use self-etching primers (see below). On etching the dentine surface, a dense network of collagen 10 to 15 µm deep is exposed (Figure 2). This becomes penetrated by the resin components of the bonding system or by the acetone-containing primers of systems which use these to form the 'hybrid' layer.⁸

Excessive etching may produce deeper decalcification, but it might not be possible for the resin to penetrate this deeper layer and 'internal' leakage

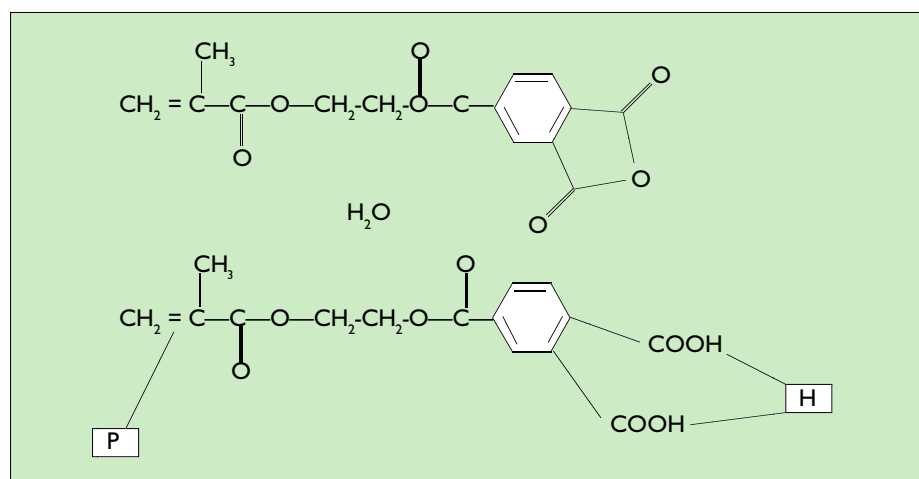


Figure 4. 4-META (4-methacryloxyethyl trimellitic anhydride). This hydrolyses readily to form an acid, as shown in the lower formula. H = hydrophilic group; P = polymerizable group.

(known as nanoleakage), resulting in failure under loading, may occur: manufacturers' suggested etching times should therefore be followed studiously. Sclerosed dentine should be etched for slightly longer than advised; alternatively, the surface layer of sclerosed dentine should be removed.¹²

'Total etch'—the use of the same etchant for enamel and dentine—is now widely used.²⁰ This has the advantage of simplicity and will save time if both enamel and dentine can be treated simultaneously.

Primer

In contrast to conditioners, which are removed from the dentine surface, primers (or adhesives) are applied to the conditioned surface and left *in situ*. The function of a primer is to act as a link or 'bridge' between the dentine and the restorative resin. Thus primers are designed to be bifunctional, containing one or more substances, each of which has two different types of functional molecular groups. Primer molecules possess hydrophilic groups (for example, carboxylate or phosphate) which have an affinity for wet dentine, and polymerizable groups (carbon-carbon bonds) which can react with the restorative resin. Some examples are shown in Figures 3 and 4. Note that some formulations contain HEMA (Figure 1). This is polymerizable, and is hydrophilic by virtue of its hydroxyl group.

Resin

The resin component of a bonding system normally consists of a combination of resins such as *bis*-GMA and/or other dimethacrylate resins. These penetrate the primed dentine and copolymerize with the primer to form an interpenetrating *hybrid* layer of collagen and resin. In most systems the resin is unfilled, although systems which include a filler in their resin are considered to have advantages—such as no 'white line' at restoration margins. It is also said that the partially filled resin layer acts as a shock absorber.

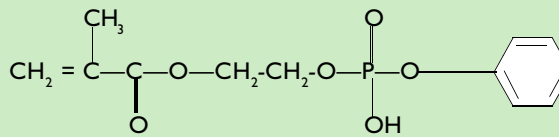


Figure 5. Phenyl-P, 2-(methacryloxy)ethyl phenyl hydrogen phosphate.

One-Bottle Bonding Systems and Self-Etching Primers

One early dentine bonding system required the operator to carry out up to seven stages during the bonding procedure. As it may be considered that the greater the number of stages, the greater the potential for error, manufacturers have sought to reduce the number of stages. While fourth-generation systems generally require the application of etchant, primer and bonding resin, most recent attempts to further reduce the number of stages to two have taken manufacturers down one of two routes: the 'one-bottle' bonding systems and the 'self-etching' primers.

One-Bottle Bonding Systems

In these systems the primer and resin, which are often based on previous materials, are combined to produce a 'one-bottle' or 'one-stage' bonding system. However, etching is required before application of the resin, so these are not truly *one* bottle systems.

Self-Etching Primers

In these systems the etchant and primer are combined. One such system (Clearfil Liner Bond 2: Kuraray Co. Ltd., Osaka, Japan) contains phosphate derivatives of hydrophilic monomers, one example being the acidic adhesive monomer phenyl-P (Figure 5). In Clearfil Liner Bond 2, phenyl-P is present at a concentration of 20 to 25%, and at this concentration in the presence of water the solution is very acidic (pH approx. 1.5). The self-etching primer solutions also may contain up to 50% HEMA or other hydrophilic monomers, so that they simultaneously etch and prime the

dentine. Self-etching primers must have sufficient acidity to overcome the buffering potential of the dentine, but they must also contain sufficient monomer to compete with water when they diffuse through the smear layer. However, the acidity of the primer may be reduced as it penetrates the smear layer, leaving less acid to etch the underlying dentine. As the smear layer might not be totally removed by these systems, the partially demineralized smear layer becomes incorporated into a hybrid layer, which may explain why self-etching primers, in general, produce thinner hybrid layers than systems using etchants such as phosphoric acid.²¹ However, this does not appear to result in any deficiency in bond strength.

Contemporary systems may employ a reduced number of bottles as described above but these 'one-step' systems often require repeated applications of a particular stage, and the total application procedure is therefore not necessarily faster or simpler than fourth-generation systems.

THE BONDING MECHANISM

Work carried out by Nakabayashi in 1982 using the resin 4-META and a 10% citric acid/3% ferric chloride conditioner (10/3) identified a boundary between dentine and resin and a diffuse transition zone approximately 5 mm thick between the resin phase and the underlying mineralized dentine.⁹ This layer was termed the hybrid layer, resin-reinforced zone or resin-infiltrated layer (Figure 2). It has been considered to provide a strong union between resins and dentine. Its formation requires removal of the smear layer and

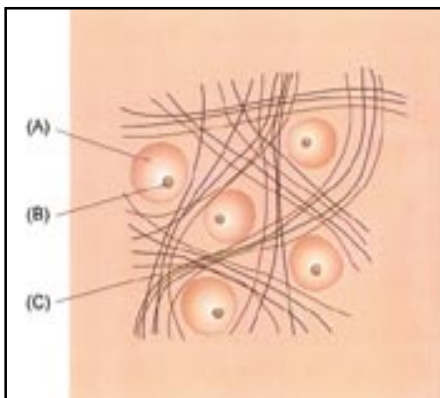


Figure 6. Structure of dentine: **A** peritubular dentine; **B** dentinal tubule; **C** collagen fibres of the intertubular dentine.

smear plugs, stabilization of the collagen network (which can collapse if desiccated) and application of a suitable monomer mixture that facilitates the diffusion or permeation of resin into the demineralized but stabilized dentine matrix. Although the first smear layer was produced using the resin 4-META following treatment with 10/3, similar smear layers have been observed with many contemporary dentine bonding systems. Formation of hybrid layers occurs principally in the intertubular dentine (Figure 6).

The effectiveness of bonding resin coupling agents is generally considered to be primarily a function of penetration into conditioned dentine. However, the significance of the hybrid layer has recently been questioned, since experiments in which collagen is dissolved from a decalcified dentine surface using hypochlorite solutions have not always demonstrated a decrease in bond strength after removal of the collagen layer.^{22,23} This is particularly apparent with systems that are based on an acetone carrier. Results of recent work by Inai and co-workers have indicated a decrease in shear bond strengths to hypochlorite-treated surfaces for Scotchbond MP and Scotchbond 1 (3M, St. Paul, MN, US) while Prime & Bond 2.1 (Dentsply, Weybridge, UK) and One-Step (Bisco Inc., Itasca, IL, US), both acetone-based materials, did not show a

significant decrease.²⁴ These results have been confirmed by Kanca.²³ The mechanism for this is not particularly understood, but a number of possible causes may be postulated:

- the materials with a diminution of bond strength could be more prone to inhibition of polymerization by the hypochlorite-treated surface;
- materials that do not show a decrease in bond strength are sufficiently acidic to etch the hypochlorite-treated dentine surface;
- when the collagen is removed by the hypochlorite, the remaining surface may be sufficiently retentive micromechanically to bond with some materials;
- the demineralized collagen layer does not contribute to the strength of adhesion with some materials.

Further research is needed to provide a more complete understanding of the bonding mechanism on collagen-poor dentine.

Intertubular Bonding

The hybrid layer has been considered to provide micromechanical bonding of resin to dentine, but resin tag formation may also contribute to the overall bond strength, especially if penetration of the lateral channels that join individual dentinal tubules can be achieved. By this means, penetration of tubules may generate mechanical retention as there will be no possible path of withdrawal unless some of the tags fracture. However, this mechanism for bonding can play a major role in a dentine surface only where dentinal tubules are present in large numbers (i.e. in areas of dentine nearer to the pulp).

Wet Bonding

For dentists who qualified more than 10 years ago, the notion of placing a restoration on a surface that is wet probably conflicts with all their training. This may apply especially to bonding procedures, given that early

bonding systems were highly hydrophobic and the presence of water was therefore inappropriate. However, research by Kanca in 1992 questioned this concept and demonstrated, when using the All Bond 2 system (Bisco, Itasca, IL, US), that increased bond strengths could be achieved when the dentine surface was moist rather than dry.²⁵

Water may arise from dentinal tubule fluid, atmospheric water, rinsing procedures and adhesive solutions, so the question 'how wet is wet?' must be answered. Currently available systems are likely to contain hydrophilic resins such as HEMA and are therefore much more tolerant of moisture than their predecessors. In general, therefore it appears that the dentine surface should be left moist and not desiccated. This is explained by the fact that the collagen network left by the decalcification of the dentine surface may collapse if desiccated: it is necessary to prevent collapse by keeping the dentine surface moist or by the application of a suitable monomer mixture that facilitates the permeation of resin.

Wet bonding has also been shown to improve significantly the marginal seal of restorations in which an acetone-based primer is used.²⁶ However, large amounts of water on the dentine surface may interfere with bonding—this is termed the 'overwet phenomenon'.²⁷

Systems that contain acetone as a carrier may tolerate more moisture on the dentine surface without detriment to bond strength; other systems (especially those containing ethanol, such as Scotchbond Multipurpose; 3M) require the dentine surface to be blot dried and not desiccated. In acetone-containing systems, when the acetone primer contacts the water on the dentine, the boiling point of the acetone is raised and the boiling point of the water is lowered, a process known as azeotrophism.²⁸ This causes the evaporation of both the acetone and the water, and the resin is left behind.

It is important to note that the production of a wet surface does not imply a tolerance for contaminants such as blood, gingival crevicular fluid,

Name	Manufacturer	Components	Composition
Scotchbond I	3M Dental, St Paul, MN, USA	Conditioner Primer/adhesive	35% phosphoric acid bis-GMA, HEMA, water, ethanol, dimethacrylates, methacrylate, copolymer of polyacrylic and polyitaconic acids
One-Step	Bisco, Itasca, IL, USA	Conditioner Primer/adhesive	32% phosphoric acid BPDM, bis-GMA, HEMA, acetone
Prime & Bond 2.1	Dentsply, Milford, DE, USA	Conditioner Primer/adhesive	34% phosphoric acid, dimethacrylates, including PENTA, acetone
Optibond Solo	Kerr Products, MI, USA	Conditioner 3 Primer/adhesive	35% phosphoric acid, GPDM, HEMA, bis-GMA, ethanol
Gluma One	Heraeus Kulzer, Dormagen, Germany	Conditioner Primer/adhesive	20% phosphoric acid, HEMA, UDMA, 10% 4-META
Fuji Bond LC	GC International, Leuven, Belgium	Conditioner Primer/adhesive	20% PAA, 3% aluminium chloride, RMGI, water
Syntac Sprint	Ivoclar Vivadent, Liechtenstein	Conditioner Adhesive	37% phosphoric acid 39% HEMA, 11% methacrylate, modified polyacrylic acid, 3% maleic acid, water

Table 2. The components of some fifth-generation bonding systems.

saliva or oil. In view of the wide variety of monomers and solvents in the systems currently available, it is essential that manufacturers' instructions are followed meticulously. The composition of a number of currently available dentine bonding systems is shown in Table 2.

The improved reliability of dentine bonding systems in recent years has increased their potential clinical applications. These applications will be described in a subsequent paper.

Note: Editorial decisions and peer reviewing organized by Professor Edwina Kidd.

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