Chapter 16

Bonding to Enamel and Dentin

INTRODUCTION

The traditional "drill and fill" approach is fading now because of numerous advancements taking place in restorative dentistry. For a restorative material, adhesion is the primary requirement so that restorative materials can be bonded to enamel or dentin and without the need of extensive tooth preparation. The initial advancement was made in 1956, by a pedodontist, Buonocore, who developed acid etching of the enamel. He showed that when enamel is treated with a dilute acid for 30 seconds, it results in microscopically roughened, porous surface into which the resin forms retentive tags. Dentin is different from enamel, it contains more than 25% organic material, which is mainly collagen and tissue fluid. The fluid present in dentinal tubules makes the bonding difficult. The adhesion to dentin requires decalcification of the dentinal surface to expose a layer of interlacing collagen fibrils and the entrances of the dentinal tubules. When resins are used, they form an intermediate layer with exposed spongy collagen network which can be then bonded to the retentive inner surface of the restoration by means of a resin similar to that of enamel bonding.

The past decade has seen increased use of bonding agents in concurrence with traditional dental materials. The availability of adhesive techniques permits the placement of aesthetic restorations like composite resins, aesthetic inlays and veneers, etc. Though a wide range of adhesives is available but there are some requirements which a dental adhesive should possess.

ADHESIVE DENTISTRY

Following factors have shown to be responsible for boost in adhesive dentistry:

1. The development of tooth colored restorative materials.
2. The introduction of new composite resins with superior properties.
3. Advances in the development of adhesive systems.
4. Increased concern among patients for aesthetics and tooth colored restorations.

Indications for Use of Adhesives

- To treat carious and fractured tooth structure.
- To restore erosion or abrasion defects in cervical areas.
- To correct unaesthetic contours, positions, dimensions, or shades of teeth.
- To treat dentinal hypersensitivity.
- For the repair of fractured porcelain, amalgam and resin restorations.
- For pit and fissure sealants
- To bond composite restorations
- To bond silver amalgam restorations.
- To lute crowns.
- To bond orthodontic brackets.

Advantages of Bonding Techniques

The following are advantages of bonding systems:

1. Adhesion of composite resin restorations to enamel and dentin.
2. Minimizes removal of sound tooth structure.
3. Management of dentin hypersensitivity.
4. Adhesion reduces microleakage at tooth restoration interface.
5. As a part of resin cements for bonding cast restorations.
6. Adhesion expands range of aesthetic possibilities.
7. Bonding of porcelain restorations, e.g. porcelain inlays, onlays and veneers.
8. Reinforces weakened tooth structure.
9. Reduction in marginal staining.
10. For repair of porcelain or composite.
11. Bonding amalgam restorations to tooth.
12. Repair of amalgam restorations.
13. To bond orthodontic appliances.

History

1955	Buonocore applied acid to tooth to render the tooth more receptive to adhesion.
1956	First commercially available bonding agent (NPG-GMA).
1978	Second generation adhesives introduced.
1980's	Total etch concept gains acceptance.
1982	Hybrid layer concept by Nakabayashi
1990's	Multistep and one step adhesive systems.

Definitions

Adhesion or bonding: The forces or energies between atoms or molecules at an interface that hold two phases together.

Adherend: The surface or substrate that is adhered **(Fig. 16.1)**.

Adhesive/adherent: A material that can join substances together, resist separation and transmit loads across the bond **(Fig. 16.1)**.

Adhesive failure: The bond that fails at the interface between the two substrates.

Cohesive failure: The bond fails within one of the substrates, but not at the interface.

Adhesion can occur by

1. Chemical means
2. Physical means
3. Mechanical means

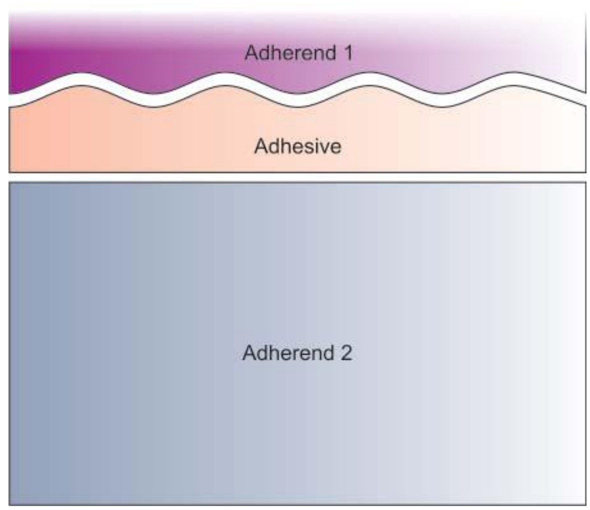
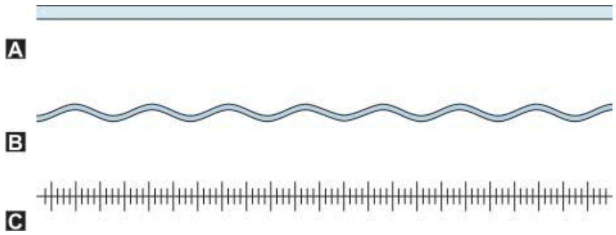


Fig. 16.1: Diagrammatic representation of dental adhesive system, where Adherend 1 is enamel, dentin or both. Adhesive is bonding agent, Adherend 2 is composite resin

Mechanism of Adhesion (Figs 16.2A to C)

1. ***Physical means of adhesion*** involve the:
   a. *Van der Waals interactions:* Attraction between opposite charges on ions and dipoles.
   b. *Dispersion forces:* Interaction of induced dipoles
   c. *Hydrogen bond:* It is a particularly strong bond and can be included among physical forces.
2. ***Chemical means of adhesion*** involves primary forces that is:



Figs 16.2A to C: (A) Physical bonding (B) Mechanical bonding (C) Chemical bonding

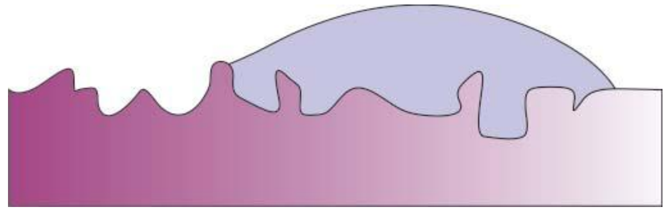


Fig. 16.3: A good wetting ensures good adhesion

a. *Covalent bond:* It involves sharing electron between two atoms or molecules. It represents strong bonds. Formation of covalent bond liberates considerable energy. Covalent bond is present in all organic compounds.
b. *Ionic bond:* It involves an actual transfer of electrons from one atom to another. For example, ion exchange adhesion mechanism in GICs.
c. *Metallic bond:* It is the chemical bond characteristics of metals in which mobile electrons are shared among atoms in a usually stable crystalline structure.

3. ***Mechanical means of adhesion:*** Here the bonding occurs because of penetration of one material into another at the microscopic level. For example, in composite resins the bonding involves the penetration of resin into enamel and dentin and formation of resin tags.

Adhesion forces across different materials depend on

- Physical and chemical properties of both adhesive and the adherent.
- Homogeneity.
- Thickness of interface.
- Oral environment with its moisture.
- Chewing habits.

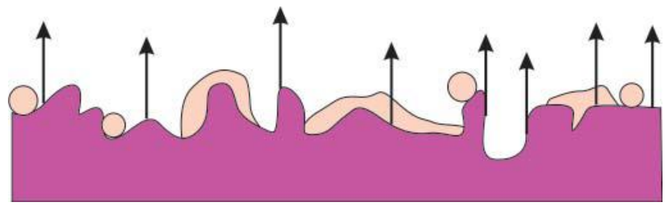


Fig. 16.4: A clean surface increases the adhesion

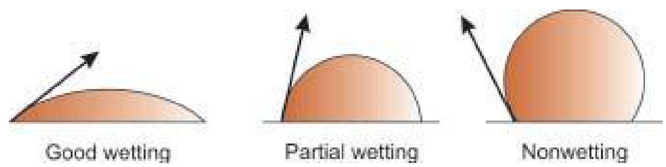


Fig. 16.5: Lesser is the contact angle, better is the adhesion

Factors Affecting Adhesion

Wetting

Wetting is an expression of the attractive forces between molecules of adhesive and adherent. In other words, it is the process of obtaining molecular attraction **(Fig. 16.3).** Wetting ability of an adhesive depends upon two factors:

- ***Cleanliness of the adherend (Fig. 16.4):*** Cleaner is the surface, greater is the adhesion.
- ***Surface energy of the adherend:*** More the surface energy, greater is adhesion.

Contact Angle (Fig. 16.5)

Contact angle refers to the angle formed between the surface of a liquid drop and its adherent surface. The stronger the attraction of the adhesive for the adherent, the smaller will be the contact angle. The zero contact angle is the best to obtain wetting.

Surface Energy

Generally, harder the surface, higher is the surface energy, higher is the adhesive property of material. The surface tension of the liquid and the surface energy of the adherend, ultimately determine the degree of wetting that occurs.

Surface Contamination

Substrate surface should be clean as the contamination prevents the adhesion. Adhesive should be able to fill the irregularities making the surface smooth allowing proper or intimate contact **(Fig. 16.6)**.

Water: Higher is the water content, poorer is the adhesion. Water can react with both materials by the high polar group and hydrogen bond which can hamper the adhesion.

ENAMEL BONDING

Enamel, the hardest tissue in the human body consists of 95% mineralized inorganic substance, hydroxyapatite

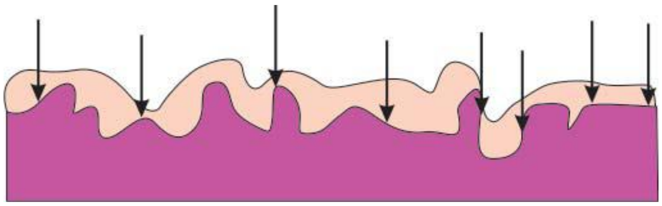
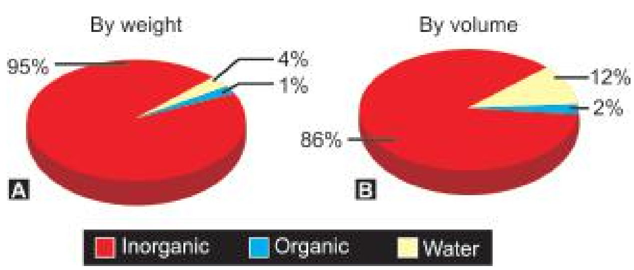


Fig. 16.6: There should be intimate adaptation between two surfaces for optimal bonding

arranged in a dense crystalline structure and a small amount of protein and water **(Figs 16.7A and B)**. To bond to enamel, it is very important to focus on the mineral component (hydroxyapatite) of enamel. Buonocore, in 1955, was first to reveal the adhesion of acrylic resin to acid etched enamel. He used 85% phosphoric acid for etching, later Silverstone revealed that optimum concentration of phosphoric acid should range between 30-40% to get a satisfactory adhesion in the enamel. Usually 37% phosphoric acid is used for 15 to 30 seconds **(Fig. 16.8)**. If the concentration is greater than 50 percent, then monocalcium phosphate monohydrate may get precipitated while at concentrations lower than 30 percent, dicalcium phosphate monohydrate is precipitated which interferes with adhesion.



Figs 16.7A and B: Composition of enamel (A) By weight (B) By volume

Fig. 16.8: Etchant

Several changes have taken place regarding the acid etching of enamel surfaces. These include:

- ***Development of phosphoric acid gels:*** Gels provide the clinician a greater control and precision in the placement of etching agents **(Fig. 16.9)**. Earlier most gel etchants used to contain silica as a thickening agent. But recently available gels employ polymeric thickening agents which have better wetting abilities and rinse off more easily than silica containing gels.
- ***Percentage of etchants used:*** Currently used etchants employ the concentrations of phosphoric acid that ranges from 10 to 50%. Studies have shown no difference in etching of enamel using higher concentration or lower concentrations of acid. Use of lower concentrations of phosphoric acid and reduced etching time has shown to give an adequate etch of the enamel while avoiding excessive demineralization of the dentin.
- ***Decrease in the acid application time:*** The standard treatment protocol for the etching of enamel has been application of 37% phosphoric acid for 60 seconds. But studies show that enamel should not be etched for more than 15-20 seconds. If enamel is etched for more than required time, deeper etch of the enamel surface occurs. Since a bonding agent has a high viscosity, the surface tension effect of the agent would not allow full penetration of the etched enamel. This will result in a 'dead space' beyond the bonded area. When enamel bends, or the weak resin based bond breaks off, the dead space becomes exposed to oral fluids which has lower surface tension and thus penetrates the dead space. This may result in secondary caries or discoloration of the margins.

Fig. 16.9: Etching gel provides greater control and precision in the etchant placement

Use of acid conditioners (i.e. nitric, citric, oxalic, maleic acids) other than traditional phosphoric acid:
Many acids have been developed recently for conditioning like nitric acid, citric acid and oxalic acids. These acids cause mild etching/conditioning, so for total etching it is advisable to use phosphoric acid.

Abbreviations commonly used for resin chemicals	
• Bis-GMA	Bisphenol glyceryl methacrylate
• HEMA	2-Hydroxyethyl methacrylate
• TGDMA/ TEGDMA	Triethylene glycol dimethacrylate
• 4-META	4-Methacryloxyethyl trimellitate anhydride
• UDMA	Urethane dimethacrylate
• PMDM	Pyromellitic acid diethyl methacrylate
• NPG-GMA	N-phenylglycine glycidyl methacrylate
• GPDM	Glycerophosphoric acid dimethacrylate
• EDTA	Ethylene diamine tetraacetic acid

Conditioning

It is the process of cleaning the surface and activating the calcium ions, so as to make them more reactive.

Etching

It is the process of increasing the surface reactivity by demineralizing the superficial calcium layer and thus creating the enamel tags. These tags are responsible for micromechanical bonding between tooth and restorative resin.

Steps for Enamel Bonding

- Perform oral prophylaxis procedure using non-fluoridated and oil less prophylaxis pastes.
- Clean and wash the teeth with water. Isolate to prevent any contamination from saliva or gingival crevicular fluid.
- Apply acid etchant in the form of liquid or gel for 10 to 15 seconds. Deciduous teeth require longer time for etching than permanent teeth because of presence of aprismatic enamel in deciduous teeth.
- Wash the etchant continuously for 10 to 15 seconds.
- Note the appearance of a properly etched surface. It should give a frosty white appearance on drying.
- If any sort of contamination occurs, repeat the procedure.
- Now apply bonding agent and low viscosity monomers over the etched enamel surface. Generally, enamel bonding agents contain BISGMA or UDMA with TEGDMA which is added to lower the viscosity of the bonding agent. The bonding agents due to their low viscosity, rapidly wet and penetrate the clean, dried, conditioned enamel into the microspaces forming resin tags. The resin tags which form between enamel prisms are known as Macrotags **(Fig. 16.10)**.
- The finer network of numerous small tags are formed across the end of each rod where individual hydroxyapatite crystals were dissolved and are known as microtags. These microtags are more important due to their larger number and greater surface area of contact. The formation of resin micro and macro tags within the enamel surface constitute the fundamental mechanism of enamel-resin adhesion.

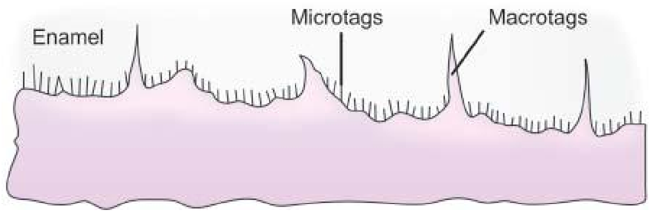


Fig. 16.10: Formation of microtags and macrotags when bonding agent is applied to etched tooth surface

Mechanism of Etching

Etching of enamel produces a number of effects:

1. Cleanses debris from enamel.
2. Produces a complex three-dimensional microtopography at the enamel surface
3. Increases the enamel surface area available for bonding.
4. Produces micropores into which there is mechanical interlocking of the resin **(Fig. 16.11)**.
5. Exposes more reactive surface layer, thus increasing its wettability.

When seen microscopically, three types of enamel etching patterns are seen:

Type I Preferential demineralization of enamel prism core leaving the prism peripheries intact. Here corresponding tags are cone shaped.

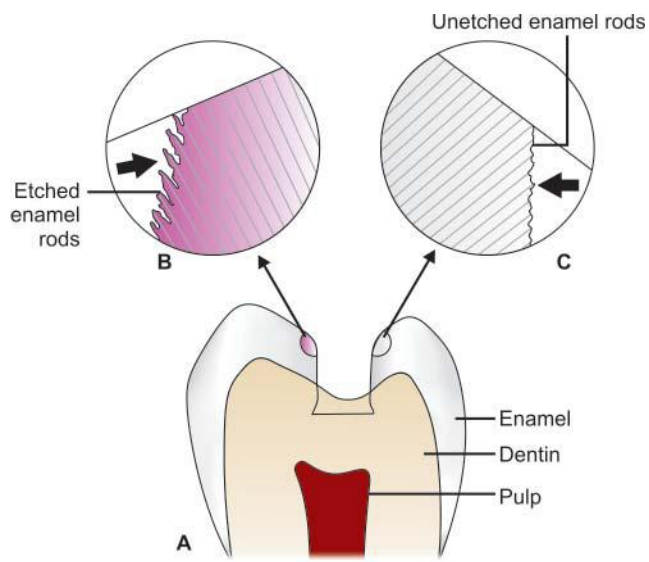


Fig. 16.11: Difference in appearance of etched and unetched enamel rods

Type II There is preferential removal of inter prismatic enamel leaving the prism cores intact. The corresponding enamel tags are cup shaped.

Type III In this, the pattern is less distinct, including areas that resemble type I and II patterns and areas which bear no resemblance to enamel prism.

Basically, acid etching creates a 5-50 micron deep microporous layer into which adhesive resin flows. This result in a longlasting enamel bond achieved via micro-mechanical interlocking between the resin and enamel. Bond strength of etched enamel to composite resin usually varies between 15-25 MPa.

Among the factors that affect bonding of enamel are its fluoride content, arrangement of crystals and impurities, e.g. presence of magnesium and carbonates in the hydroxyapatite crystals.

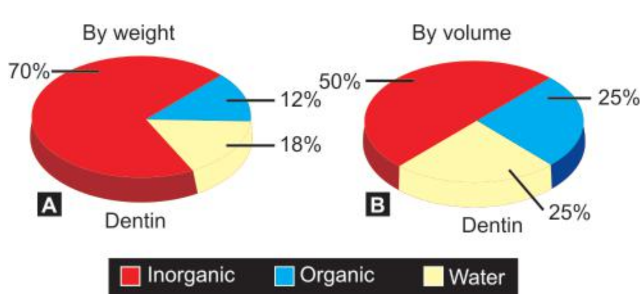
Factors affecting effects of acid etching on enamel

- Form of acid used that is solution or gel
- Concentration of acid used and time of etching
- Type of acid used
- Chemical nature of enamel
- Whether enamel is fluoridated or demineralized
- Type of dentition, i.e. primary or permanent

DENTIN BONDING

Bonding to dentin has been proven more difficult and less reliable and predictable than to enamel. This is basically because of difference in morphologic, histologic and compositional differences between the two:

- In enamel, it is 95% inorganic hydroxyapatite by volume, in dentin it is 50%. Dentin contains more water than does enamel **(Fig. 16.12)**
- Hydroxyapatite crystals have regular pattern in enamel whereas in dentin, hydroxyapatite crystals are randomly arranged in an organic matrix.
- The presence of the smear layer makes wetting of the dentin by the adhesive more difficult.



Figs 16.12A and B: Composition of dentin (A) By weight and (B) By volume

- Dentin contains dentinal tubules which contain vital processes of the pulp, odontoblasts. This makes the dentin a sensitive structure.
- Dentin is a dynamic tissue which shows changes due to aging, caries or operative procedures.
- Fluid present in dentinal tubules constantly flows outwards which reduces the adhesion of the composite resin to dentin bond.

Dentin bond strength is quite variable because it is dependent upon following factors:

- Different quality of dentin including the number, diameter and size of dentinal tubules in deep and superficial dentin **(Fig. 16.13)**: Dentin permeability is not uniform throughout the tooth, it is more in coronal dentin than root dentin. There are differences within coronal dentin also. Since tubules are more numerous and wider near pulp, there is more fluid and less intertubular dentin, this makes dentin bonding less effective in deeper dentin than superficial dentin.
- Amount of collagen: As dentin ages, there is increase in mineralization, the ratio of peritubular/intertubular dentin and decrease in the number of dentinal tubules which overall affects the adhesion quality of dentin.

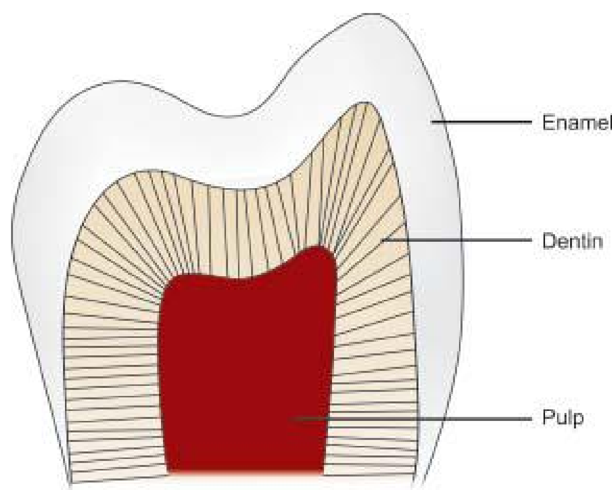


Fig. 16.13: Difference in dimensions and quantity of dentinal tubules in deep and superficial dentin

Conditioning of Dentin

For removal or modification of smear layer, many acids or/and calcium chelators are used:

1. *Acids:* Commonly used acid for conditioning dentin is 37% phosphoric acid. It not only removes the smear layer but also exposes microporous collagen network into which resin monomer penetrates. Usually, it forms

exposed collagen fibrils which are covered with amorphous layer, a combination of denatured collagen fibers and collapsed residual collagen layer. This is collagen smear layer which is resistant to monomer penetration.

It is always preferred to maintain conditioned dentin in moist state so as to prevent the collapse of unsupported collagen fibers.

Other acids used for dentin conditioning are nitric acid, maleic acid, citric acid, oxalic acid and hydrochloric acid.

2. ***Calcium chelators:*** These are used to remove and/or modify the smear layer without demineralizing the surface dentin layer. Commonly used chelator is ethylene diamine tetraacetic acid (EDTA).

Priming of Dentin

Primers are agents which contain monomers having hydrophilic end with affinity for exposed collagen fibrils and hydrophobic end with affinity for adhesive resin. Commonly used primers have HEMA and 4-META monomers, dissolved in organic solvents.

Primers are used to increase the diffusion of resin into moist and demineralized dentin and thus optimal micromechanical bonding. For optimal penetration of primer into demineralized dentin, it should be applied in multiple coats. Also it is preferred to keep the dentin surface moist, otherwise collagen fibers get collapsed in dry condition resisting the entry for primer and adhesive resin.

Moist vs Dry Dentin

Collagen is one of the important factors in determining the dentin bonding. By etching of dentin, removal of smear layer and minerals from dentin structure occurs, exposing the collagen fibers **(Fig. 16.14)**. Areas from where minerals are removed are filled with water. This water acts as a plasticizer for collagen, keeping it in an expanded soft state. Thus, spaces for resin infiltration are also preserved. But these collagen fibers collapse when dry and if the organic matrix is denatured **(Fig. 16.15)**. This obstructs the resin from reaching the dentin surface and forming a hybrid layer.

Thus, the desired effect of acid etching, which is increased permeability, is lost. For this reason, presence of moist/wet dentin is needed to achieve successful dentin bonding. When primer is applied to wet/moist dentin, water diffuses from the primer to the organic solvent and the solvent diffuses along with the polymers into the demineralized dentinal matrix and tubules. Sensitivity to dry or moist dentin varies according to the type of solvent used for the primer resin.

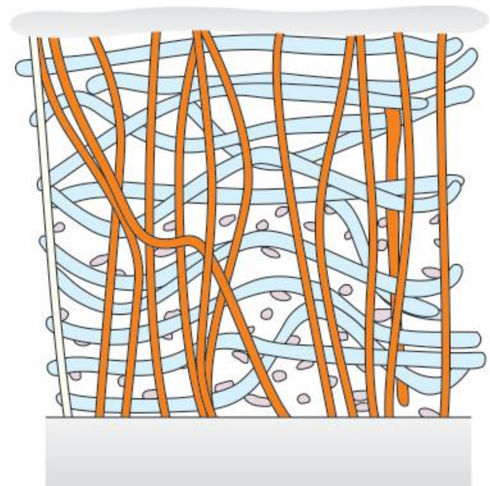


Fig. 16.14: Etching of dentin causes exposure of collagen fibrils. Interfibrillar water acts as plasticizer and keep the fibers open

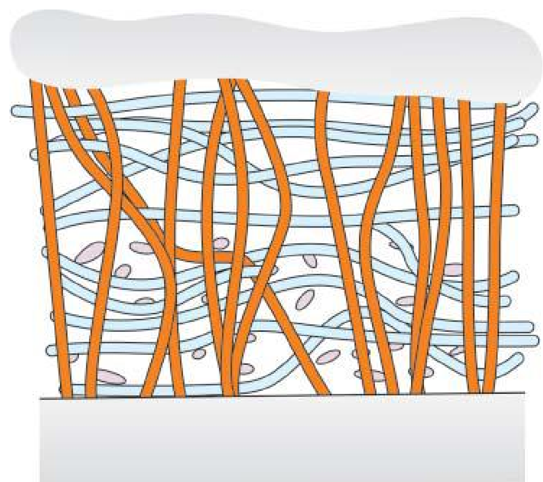


Fig. 16.15: In dehydrated dentin, loss of water causes collapse of collagen fibrils which prevent penetration of monomer

Reasons for better bonding in moist dentin

1. The acetone trails water and improves penetration of the monomers into the dentin for better micromechanical bonding.
2. Water keeps collagen fibrils from collapsing, thus helping in better penetration and bonding between resin and dentin.

Wet Bonding

In this, primers consisting of hydrophilic resin monomers dissolved in water miscible organic solvents like ethanol and acetone are used.

Acetone-based primers are dependent on a moist dentin surface for hybridization because the acetone displaces water present in the interfibrillar spaces of the collagen network and carry hydrophilic resin alongwith it for hybridization.

Dry Bonding

In this, water-based primers are used. Water-based primers are not dependent on moist dentin because of their ability to self-wet a dried dentin surface and thus separating the collapsed collagen fibers.

As we have seen that moist dentin is friendly with all primer types, so it is advisable to have moist dentin for resin-dentin bonding. To get moist dentin after etching, do not dry the dentin with compressed air after rinsing away etchant. Instead use high-volume evacuation to remove excess water and then blot the remaining water present on the dentin surface using gauze or cotton to leave dentin optimally moist.

If the dentin surface is made too dry, there will be collapse of the collagen fibers and demineralized dentin **(Fig. 16.16)**. This results in low bond strength because of ineffective penetration of the adhesive into the dentin.

If the dentin surface is too wet,

- One cannot check for enamel "frosted" etch appearance.

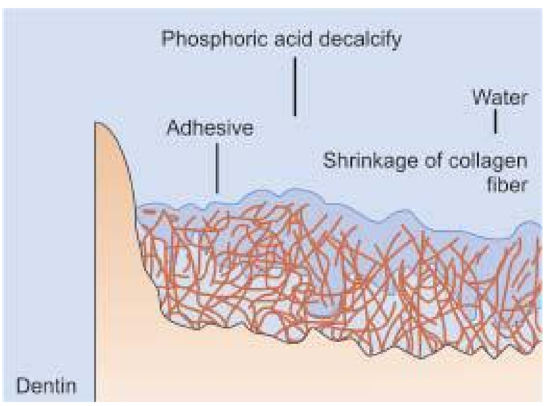


Fig. 16.16: Overdrying of dentin causes collapse of collagen fibers and thus ineffective penetration of adhesive

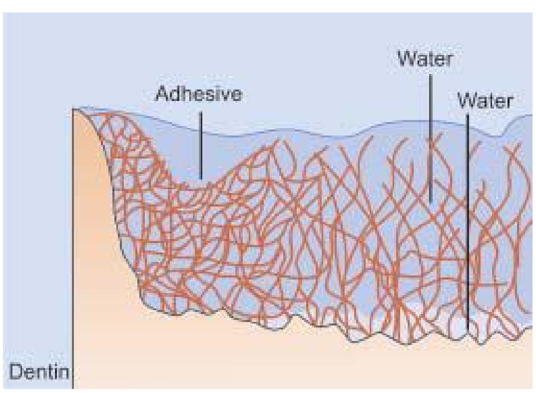


Fig. 16.17: If dentin is overwet, presence of water dilutes the monomer and competes it for sites in collagen network. This lowers the bond strength

- There is reduction in bond strength because:
  1. Presence of water droplets dilute resin primer and out-compete it for sites in the collagen network which prevents hybridization **(Fig. 16.17)**
  2. The phase changes occur in the ethanol or acetone based resins.

DENTIN BONDING AGENT

Mechanism of Bonding

Dentin adhesive molecule has a bifunctional structure:

M————————R————————X

Where,

M is the double bond of methacrylate which copolymerizes with composite resin.

R is the spacer which makes molecules large.

X is functional group for bonding which bonds to inorganic or organic portion of dentin.

Ideally a dentin bonding agent should have both hydrophilic and hydrophobic ends. Hydrophilic end displaces the dentinal fluid, to wet the surface. Hydrophobic end bonds to the composite resin.

Bonding to inorganic part of dentin involves ionic interaction among the negatively charged group on X (for example, phosphates, amino acids and amino alcohols, or dicarboxylates) and the positively charged calcium ions. Commonly used bonding systems employ use of phosphates.

Bonding to organic part of dentin involves interaction with Amino (–NH), Hydroxyl (–OH), Carboxylate (–COOH), Amide (–CONH) groups present in dentinal collagen. Dentin bonding agents have isocyanates, aldehydes, carboxylic acid anhydrides and carboxylic acid chlorides which extract hydrogen from the above mentioned groups and bond chemically.

A dental adhesive should

- Provide a high bond strength to enamel and dentin
- Provide an immediate bond
- Provide a durable bond
- Prevent microleakage
- Be biocompatible and nonirritating
- Be simple to use
- Be economical

Evolution of Dentin Bonding Agents

Historically, DBAs have been classified based on chemistry and the manner in which they treat the smear layer.

First Generation Dentin Bonding Systems

The first step to achieve bonding to dentin was anticipated by application of coupling agent such as glycerol-phosphoric acid dimethacrylate as a primer and N-2-hydroxy-3-methacryloxypropyl and N-phenyl phenyl glycine (NPG-GMA) and silane coupling agents. The first dentin bonding agent to appear on the market was Cervident (SS White Co, King of Prussia, PA).

These products ignored the smear layer. The mechanism of adhesion was because of deep penetration of the resin tags into the exposed dentinal tubules after etching and chelating component which could bond to the calcium component of dentin **(Fig. 16.18)**. Since they could chelate with calcium ions of the tooth structure, they formed stronger bonds with enamel than dentin. Problems with first generation bonding agents:

- Low bond strength, in the order of 2 to 3 MPa insufficient to retain the restorative material for extended periods of time.
- Loss in bond strength overtime.
- Lack of stability of individual components during storage.

Second Generation Dentin Bonding Systems

They were introduced in late 1970s. Most of the second generation bonding agents leave the smear layer intact when used but some of them employed the use of mild cleansing agents to remove smear layer **(Fig. 16.19)**. They achieved the bond strengths ranging from about 4.5 to 6 MPa.

Three types of second generation products were made available:

Etched tubule dentin bonding agents: In these, bonding to dentin was attempted by etching the tubules with 25% citric acid and then making use of ethylmethacrylate to mechanically interlock with the etched tubules.

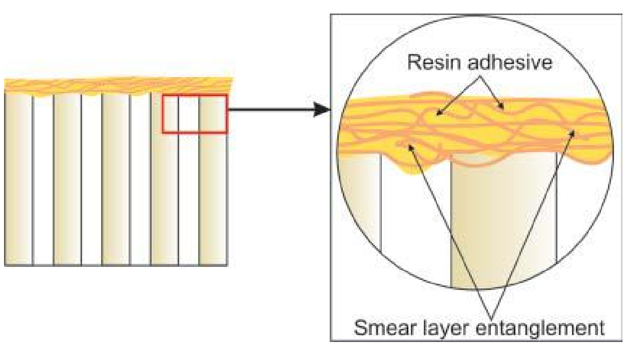


Fig. 16.18: First generation bonding agents ignored the smear layer. The bonding occurred because of deep penetration of resin tags into open dentinal tubules

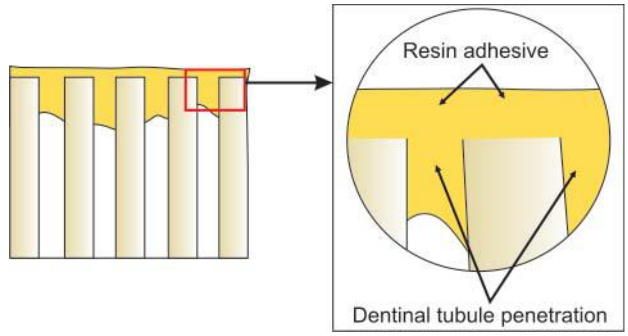


Fig. 16.19: Second generation bonding agents involve complete removal of smear layer and penetration of resin in open tubules

Phosphate ester dentin bonding agents: This system made use of a mild cleanser to modify the smear layer. These bonding agents used analogs of Bis-GMA with attached phosphate esters. The phosphate group bonded with calcium present in the tooth structure while the methacrylate end of the molecule bonded to the composite resin. These bonding agents showed 10 to 30% increase in bond strength.

Polyurethane dentin bonding agents: These bonding agents were based on the isocyanate group of the polyurethane polymer which bonds to different groups present in dentin like carboxyl, amino and hydroxyl groups.

Most of these agents used diisocyanates which simultaneously bonded to both the dentin and composite resin.

Since the setting reaction of polyurethane was not affected by the presence of fluid in the dentin tubules or smear layer, most of these systems left the smear layer intact, however some made use of hydrogen peroxide for cleansing of smear layer.

Problems with second generation bonding agents:

- Low bond strength
- Unstable interface between dentin and resin because of the insufficient knowledge about the smear layer.

Third Generation Dentin Bonding Systems

In late 1980s, the third generation DBA, two component primer/adhesive systems were introduced. In earlier used systems, conditioning step on dentin was done in conjunction with the bonding agent, but in third generation bonding system, chemistry is more diverse and various agents for modifying the dentin are used. These systems, employed the concept of conditioning and priming before application of bonding agent. In other words, in third generation systems, alteration or removal

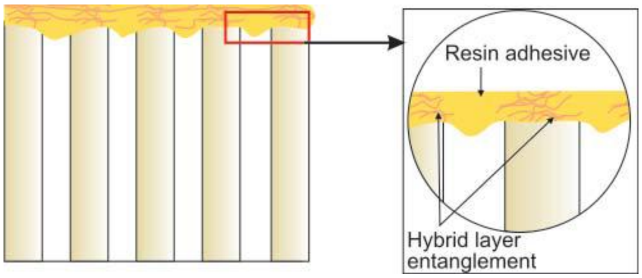


Fig. 16.20: Third generation bonding agents involved alteration/ removal of smear layer by conditioning and priming before bonding

of the smear layer is done before bonding **(Fig. 16.20)**. They are attempted it in two ways:
- Removal of smear layer without disturbing the smear plugs.
- Modifying the smear layer to improve its properties.

The application of third-generation dentin bonding agents involves three steps: etching with an acidic conditioner, priming with a bifunctional resin in a volatile solvent and bonding with an unfilled or partially filled resin.

Advantages of third generation bonding agents over first and second generation bonding agents:
- Higher bond strengths (8 to 15 MPa)
- Reduced microleakage
- Form strong bond to both sclerotic and moist dentin
- Reduced need for retention form in tooth preparation
- Can be used for porcelain and composite repairs
- Erosion, abrasion and abfraction lesions can be treated with minimal tooth preparation.

Drawbacks of third generation bonding agents:
- Decrease in bond strength with time.
- Increase in microleakage with time.

Fourth Generation Dentin Bonding Agents

They were made available in mid 1990s. Fourth generation bonding agents represent significant improvements in the field of adhesive dentistry. These agents are based on total etch technique and moist bonding concept.

Mechanism of bonding: The fourth "generation" is characterized by the process of hybridization at the interface of the dentin and the composite resin. Hybridization is the phenomenon of replacement of the hydroxyapatite and the water in the surface dentin by resin. This resin, in combination with the collagen fibers, forms a hybrid layer. In other words, hybridization is the process of resin interlocking in the demineralized dentin surface **(Fig. 16.21)**. This concept was given by Nakabayashi in 1982.

The fourth generation adhesives consist of:
1. ***Conditioner (Etchant):*** Commonly used acids are 37% phosphoric acid, nitric acid, maleic acid, oxalic acid, pyruvic acid, hydrochloric acid, citric acid or a chelating agent, e.g. EDTA.

   Use of conditioner/etchant causes removal or modification of smear layer, demineralizes peritubular and intertubular dentin and exposure of collagen fibrils.
2. ***Primer:*** Primers consist of monomers like HEMA (2-Hydroxyethyl methacrylate) and 4-META (4-Metha cryloxyethyl trimellitate anhydride) dissolved in acetone or ethanol. Thus, they have both hydrophilic as well as hydrophobic ends which have affinity for the exposed collagen and resin respectively. Use of primer increases wettability of the dentin surface, bonding between the dentin and resin and encourages monomer infiltration of demineralized peritubular and intertubular dentin.
3. ***Adhesive:*** The adhesive resin is a low viscosity, semi filled or unfilled resin which flows easily and matches

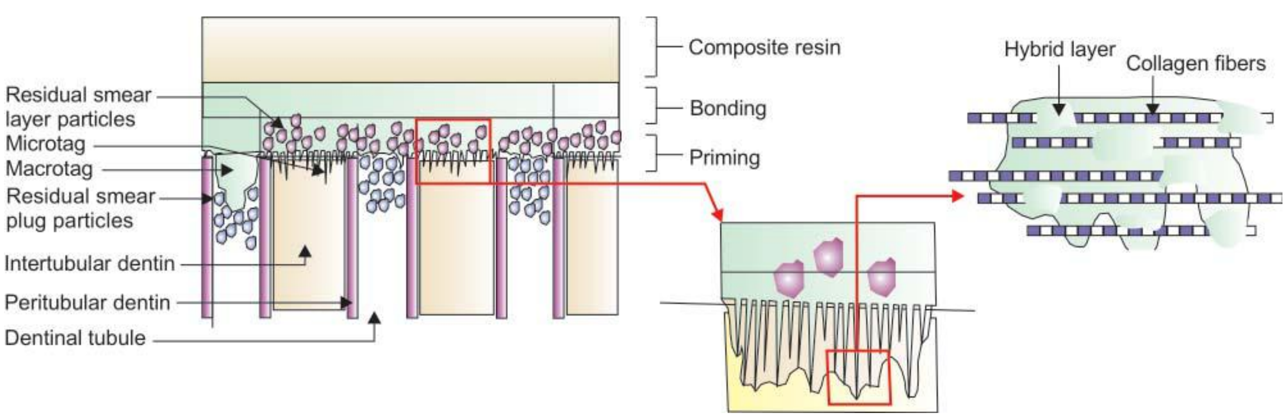


Fig. 16.21: Fourth generation bonding agents show adhesion by formation of hybrid layer

the composite resin. Adhesive combines with the monomers to form a resin reinforced hybrid layer and resin tags to seal the dentin tubules.

The following are examples of the fourth generation DBA's:

1. All bond-2 (Bisco)
2. Scotch bond multipurpose (3M)
3. Optibond FL (Kerr)
4. Clearfil liner bond 2 (Kuraray).

Advantages of fourth generation bonding agents:

- Ability to form strong bond to both enamel and dentin.
- High bond strength to dentin (17 to 25 MPa)
- Ability to bond strongly to moist dentin
- Can also be used for bonding to substrates such as porcelain and alloys (including amalgam).

Fifth Generation Dentin Bonding Agents

Fifth-generation DBAs have been available since the mid-1990s. They are also known as "one-bottle" or "one-component" bonding agents. These products are distinguished from the fourth generation bonding agents by being one-step or one-bottle products. In these agents the primer and adhesive resin are in one bottle. The first product in this category was Prime and Bond. The basic differences between the fourth and fifth generation dentin bonding agents is the number of basic components of bottles. The fourth generation bonding system is available in two bottles, one consisting of the primer and the other the adhesive, the fifth generation dentin bonding agents are available in one bottle only **(Fig. 16.22)**. This makes the fifth generation bonding agents simpler and faster than the fourth generation systems.

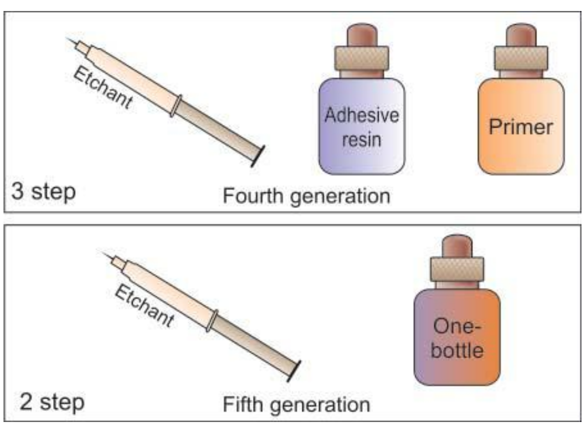


Fig. 16.22: Fourth generation bonding system is available in two bottles, one primer and other adhesive resin, while in fifth generation bonding agents, primer and adhesive are combined in one bottle only

Advantages of fifth generation bonding agents:

- High bond strength, almost equal to that of fourth generation adhesives, i.e. 20 to 25 MPa.
- Easy to use and predictable.
- Little technique sensitivity
- Reduced number of steps
- Bonding agent is applied directly to the prepared tooth surface
- Reduced postoperative sensitivity.

Disadvantages of fifth generation bonding agents:

- Lesser bond strength than fourth generation bonding agents.

The following are some of the fifth generation systems in the market.

1. Prime and Bond (Dentsply)
2. OptiBond Solo (Kerr)
3. Single Bond (3M) **(Fig. 16.23).**

Fig. 16.23: Fifth generation bonding agent

Sixth Generation Dentin Bonding Agents

They have been made available since 2000. These single bottle adhesives combine etching, priming and bonding in a single solution and as a single step. Earlier fifth-generation bonding agents were made available in single bottle consisting of both the primer and the adhesive. Before applying them, tooth structure needed to be treated with etchants. In sixth generation, they are made available with self etching primers which are used in place of the separate etchant **(Figs 16.24A to F)**. Thus etching as a separate step is eliminated. They show sufficient bond strength to dentin but poor to enamel. These use an acidified primer that is applied to the dentin and not rinsed off. Most self etching primers are moderately acidic with a pH that ranges between 1.8 and 2.5. Because of presence of acidic primer, sixth generation bonding agents do not have a long shelf life and thus have to be refreshed frequently.

Sixth generation bonding agents are further of two types:

1. Self etching primer and adhesive
   - Available in two bottles: (a) Primer (b) Adhesive
   - Primer is applied prior to the adhesive
   - Water is solvent in these systems.
2. Self etching adhesive
   - Available in two bottles: (a) Primer (b) Adhesive
   - A drop from each bottle is taken, mixed and applied to the tooth surface, for example, Prompt L-pop.

Mechanism of bonding: in these agents as soon as the decalcification process starts, infilteration of the empty spaces by dentin bonding agent is initiated **(Figs 16.24D to F)**.

Advantages of self etching primers:

- Comparable adhesion and bond strengths to enamel and dentin.
- Reduce postoperative sensitivity because they etch and prime simultaneously.
- They etch the dentin less aggressively than total etch products.
- The demineralized dentin is infiltrated by resin during the etching process.
- Since these do not remove the smear layer, the tubules remain sealed, resulting in less sensitivity.
- They form relatively thinner hybrid layer than traditional product which results in complete infiltration of the demineralized dentin by the resin monomers. This results in increased bond strength.
- Much faster and simpler technique.
- Less technique sensitive as fewer number of steps are involved for the self etch system.

Disadvantages of self etching primers:

- pH is inadequate to etch enamel, hence bond to enamel is weaker as compared to dentin.
- Bond to dentin is 18 to 23 MPa.
- Since they consist of an acidic solution, they cannot be stored and have to be refreshed.
- May require refrigeration
- High hydrophilicity due to acidic primers
- Promote water sorption
- Limited clinical data.

Total etch technique (Figs 16.24A to C)

Total etch technique involves the complete removal of the smear layer by simultaneous acid etching of enamel and dentin. According to this, smear layer is considered hurdle to adhesion because of its low cohesive strength and its weak attachment to tooth structure. After total etching, primer and adhesive resin are applied separately or together. Acid removes the dentin smear layer, raises surface energy and modifies the dentin substrate so that it can be infiltrated by subsequently placed primers and resins.

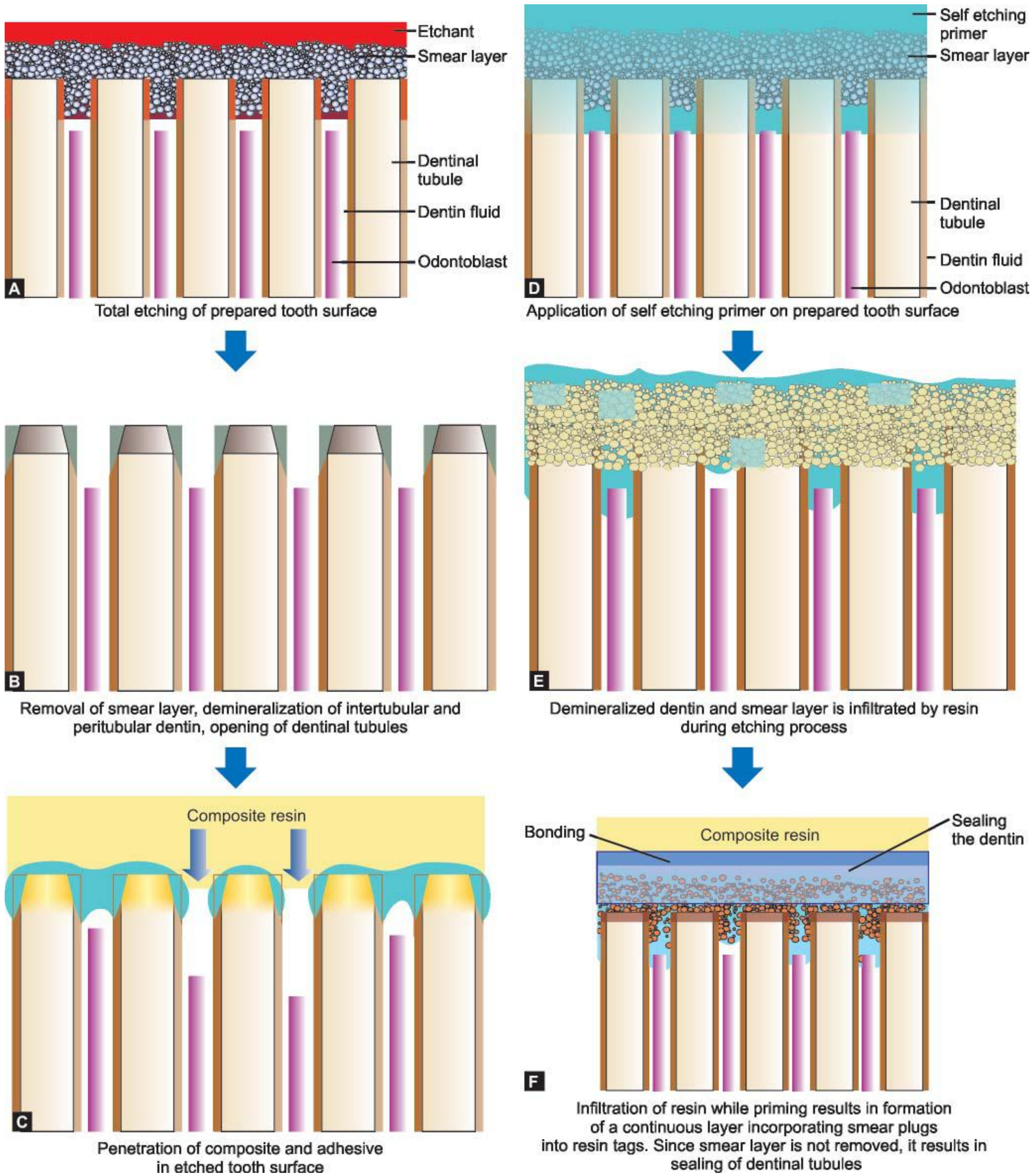
Seventh Generation Bonding Agents

They achieve the same objective as the 6th generation except that they simplified the multiple sixth generation materials into a single component, single bottle system, thus avoiding any mistake in mixing. In other words seventh generation bonding consists of only one component. Seventh generation bonding agents also have disinfecting and desensitizing properties. They provide the bond strength of 18 to 25 MPa.

Both the sixth and seventh generation adhesives are self etching, self priming adhesives which are minimum technique sensitive. The seventh generation DBAs have shown very little or no postoperative sensitivity. Example of seventh generation bonding agent is 'i Bond'.

Comparison of components of dentin bonding agents

Step	Fourth generation	Fifth generation	Sixth generation (self etch primer)	Sixth generation (self etch adhesive)	Seventh generation
1. Etching of enamel and dentin	Etchant	Etchant	Self etch primer	Self etching, self priming sealer	Self etching, self priming sealer
2. Priming of dentin	Primer	Self priming sealer	Selt etching primer	Same	Same
3. Bonding/sealing of enamel and dentin	Bonding agent	Self priming sealer	Bonding agent	Same	Same



Figs 16.24A to F: Total etch vs self-etch systems

Comparison of number of clinical steps of different dentin bonding agents		
Generation	*No. of steps*	*Steps description*
1. First	2	Etch enamel + apply adhesive
2. Second	2	Etch enamel + apply adhesive
3. Third	3	Etch enamel + apply primer + apply bonding agent
4. Fourth	3	Total etch + apply primer + apply bonding agent
5. Fifth	2	Total etch + apply bonding agent
6. Sixth	1	Apply self etch adhesive
7. Seventh	1	Apply self etch adhesive

Nanofilled Bonding Agents

These bonding agents contain extremely small filler particles. Bonding agents under this type are Prime and Bond NT (Dentsply/Caulk) **(Fig. 16.25)**.

Prime and Bond NT contains 7-nanometer fillers, greater concentration of resin and a smaller molecular weight resin.

Advantages of Using Small Fillers

- Small fillers make the bonding agent tougher and stronger.
- Covers dentin in one application
- It has shown that they penetrate dentin better
- Provide improved marginal integrity
- A low film thickness
- Satisfactory bonding to sclerotic and aged dentin.

Fig. 16.25: Nanofilled bonding agent

HYBRID LAYER AND HYBRIDIZATION

Dentin bonding agent is a low viscosity unfilled or semifilled resin for easy penetration and formation of hybrid layer. When a bonding agent is applied, partly it penetrates into collagen network, known as intertubular penetration and rest of it penetrates into dentinal tubules called intratubular penetration. In intertubular penetration, it polymerizes with primer monomer and co-polymerizes with it forming a hybrid layer/ resin reinforced layer **(Fig. 16.26)**.

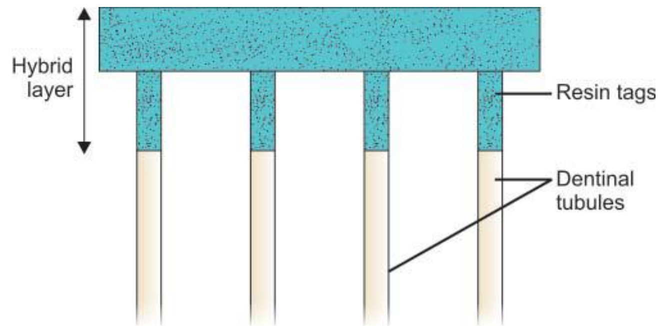


Fig. 16.26: Diagrammatic representation of hybrid layer

Hybridization (Given by Nakabayachi in 1982)

Hybridization is the process of formation of hybrid layer. Hybrid layer is phenomenon of formation of resin interlocking in the demineralized dentin surface. Hybrid layer is responsible for micromechanical bonding between tooth and the resin.

When dentin is treated with a conditioner, it exposes collagen fibril network with interfibrillar microporosities. These spaces are filled with low viscosity monomers when primer is applied. This layer formed by demineralization of dentin and infilteration of monomer and subsequent polymerization is called hybrid layer.

Zones of Hybrid Layer (Fig. 16.27)

Hybrid layer has shown to have three different zones:

1. ***Top layer:*** It consists of loosely arranged collagen fibrils and interfibrillar spaces filled with resin.

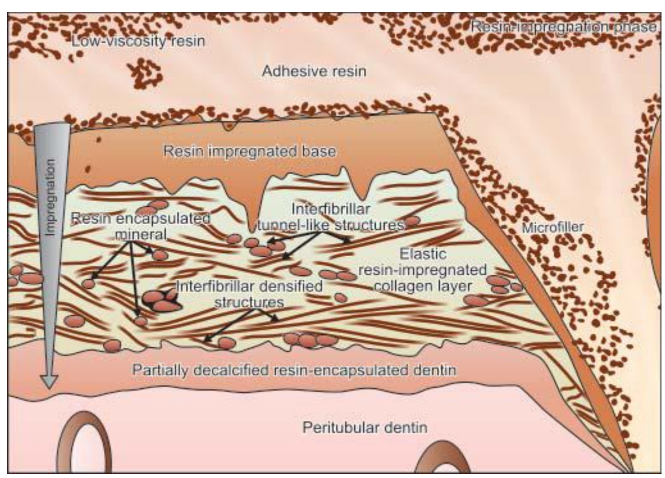


Fig. 16.27: Diagrammatic presentation of different zones of hybrid layer

2. ***Middle layer:*** It consists of interfibrillar spaces in which hydroxyapatite crystals have been replaced by resin monomer because of hybridization process.
3. ***Bottom layer:*** It consists of almost unaffected dentin with partly demineralized zone of dentin.

SMEAR LAYER

Unknown and unrecognized for years, the smear layer has become a force to be considered. The advantages and disadvantages of smear layer and whether it should be removed or not from a prepared tooth structure is still controversial. Boyde et al (1963) was first to describe the presence of smear layer on the surface of cut enamel.

Basically, when tooth surface is altered using hand or rotary instruments, cutting debris are smeared on enamel and dentin surface, this layer is called smear layer **(Fig. 16.28)**.

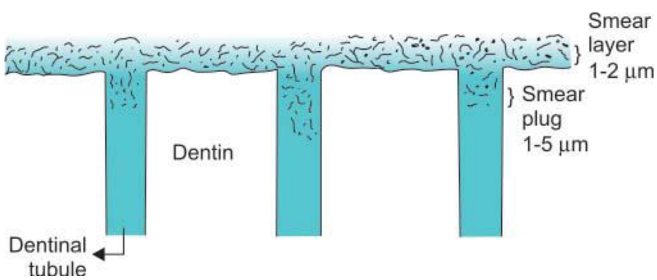


Fig. 16.28: Smear layer and smear plugs

Structure

When viewed under scanning electron microscope, smear layer has an amorphous, irregular and granular appearance. Cameron (1983) and Mader (1984) described that smear layer consists of two separate parts: one superficial and loosely attached to the underlying dentin and the other consisting of plugs of dentinal debris in the orifices of dentinal tubules **(Fig. 16.29)**.

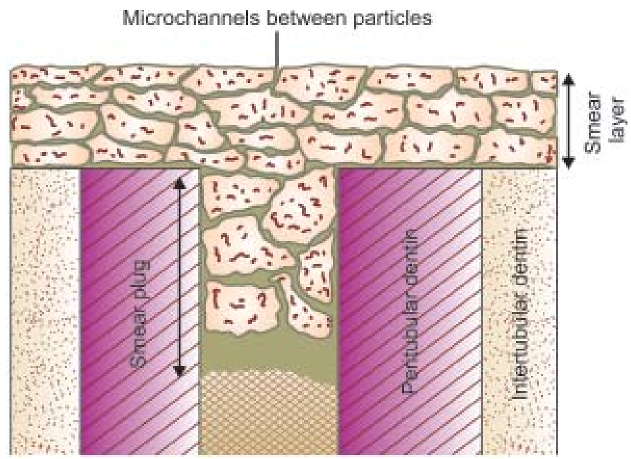


Fig. 16.29: Magnified presentation of smear layer and plugs

Depth

Smear layer has an average depth of 1 to 5 µm but in the dentinal tubules, it may go up to 40 µm.

Depth of Smear Layer Depends on Following Factors

1. Dry or wet, cutting of the dentin.
2. Type of instrument used.
3. Chemical make up of irrigating solution when doing root canal treatment.

Dentin is composed of two different layers. Superficial dentin is dentin near the enamel. Deep dentin is near the pulp. Smear layers found on deep dentin contains more organic material than superficial dentin because of greater number of proteoglycans lining the tubules or by the greater number of odontoblastic processes near pulp.

The adhesive strength of all cements is always 50% greater in superficial dentin. This may indicate that the quality and quantity of smear layer found on superficial dentin may be greater than the produced in deep dentin.

Formation of Smear Layer

When tooth structure is cut, instead of being uniformly sheared, the mineralized matrix shatters. Considerable quantities of cutting debris made up of very small particles of mineralized collagen matrix are produced. Existing at the strategic interface of restorative materials and the dentin matrix, most of the debris is scattered over enamel and dentin surfaces to form what is known as the smear layer.

Because it is a very thin layer and is soluble in acid, the smear layer will not be apparent on routinely processed specimens examined with light microscope. This may be why smear layer received so little attention by restorative dentists.

Components of Smear Layer

Smear layer consists of both organic and inorganic components.

The ***inorganic material*** in the smear layer is made up of tooth structure and some nonspecific inorganic contaminants.

The ***organic components*** may consist of heated coagulated proteins (gelatin formed by the deterioration of collagen heated by cutting temperature), necrotic or viable pulp tissue and odontoblastic processes, saliva, blood cells and microorganisms.

A profile view of the specimen may show inconsistencies, disclosing fine particulate material, densely or loosely packed to various depths into dentinal tubules.

Role of Smear Layer

Smear layer is apparently responsible for:

1. Physical barrier for bacteria and bacterial products
2. Restricting the surface area available for diffusion of both small and large molecules.
3. Resistance to fluid movement.

In vital teeth, the smear layer restricts the dentinal fluid from flushing the dentin surface. It also hinders the chemical process that produces marginal seal.

In nonvital teeth, marginal seal is improved because of the lack of moisture within dentinal tubules.

The initial sealing process occurring under amalgam restorations may be compromised because of inability of the smear layer and its penchant for leaching under amalgam. This leaching process will produce a widening of amalgam tooth microcrevice and ultimately weaken the sealing mechanism.

Disadvantages of Smear Layer

1. Bonding to the smear layer forms a weak union because smear layer can be torn away from the underlying matrix. Since this layer is nonhomogeneous and weakly adherent structure, it may slowly disintegrate, dissolving around a leaking filling material, thus creating a void.

   Studies have shown that the bond strength of a glass ionomer cement to dentin can be increased significantly by removing the smear layer.
2. Smear layers presence plays a significant part in increase or decrease in apical leakage which may be the cause of future failure of root canal fillings.
3. Smear layer on root canal walls acts as an intermediate physical barrier and may interfere with adhesion and penetration of sealers into dentinal tubules.
4. The prescence of smear layer causes possibility for leakage of microorganisms and a source of substrate for bacterial growth.
5. Presence of viable bacteria which may remain in the dentinal tubules and the use of smear layer for sustained growth and activity.

Removal of Smear Layer and its Antimicrobial Implications

Smear layer removal is a controversy that fluctuates with the various modalities of restorative dentistry.

In operative dentistry, it may depend on the type of dentin adhesive used or the use of glass ionomer.

In operative techniques, the concept of removing most of the smear layer over the tubules is an idea that is difficult to achieve clinically because of the complex geometry of many tooth preparations and the difficulty of achieving adequate success.

Inside the preparation, if the smear layer remains, it protects the pulp by plugging the tubules, preventing ingress of bacteria and their toxins as well as chemical toxins.

On the other hand, if it is removed, it allows absolute adaptation of the restoration to the true dentin surface, especially in the case of resins and amalgams. Microleakage is increased, if the smear layer remains, whereas dentin permeability is increased if the smear layer is removed.

The answer seems to lie in agents that clean the dentin surface yet leave tubules still plugged or better yet, completely clean the dentin and the tubuli orifices and then replug the tubules with a precipitate or a bonding agent.

Bonding or obturating to smear layer must be considered a weak union because the smear layer can be torn away from the underlying matrix.

Role of Smear Layer in Dentin Bonding

Smear layer may be deterrent to the bonding process, since it may serve as a barrier to the penetration of resin to the underlying dentin substrate.

Agents for Smear Layer Removal

1. ***Citric acid:*** Acid etching dentin for 60 sec with 6% citric acid removed nearly all of the smear layer as well as the surface peritubular dentin of the tubules.
2. ***Polyacrylic acid:*** It is used in combination with glass ionomer cement. An application of not more than 5 sec followed by a copious water rinse results in cleaner surface.
3. ***Chelating agent, EDTA:*** The use of chelating agents soften the smear layer allowing its successful removal. Although it is not bacteriocidal, but it is considered to be antibacterial to the extent since it eliminates the bacteria contaminated smear layer.
4. ***Maleic acid:*** Maleic acid has been in use as acid conditioner in some adhesive systems.

Smear layer removing ability of maleic acid is less in vital teeth, this could be due to the presence of the dentinal fluid which can exert pressure and so affect its complete removal.

Classification of Modern Adhesives

Basically, three adhesion strategies have been employed to modern dentin bonding agents on the basis of their interaction with the smear layer. These are:

1. Smear layer modifying agents
2. Smear layer removing agents
3. Smear layer dissolving agents.

Smear Layer Modifying Agents

In this strategy bonding agents modify the smear layer and incorporate it in the bonding process. According to these, the smear layer acts as a natural protective barrier to pulp, protecting it against bacterial penetration and also limiting the outflow of dentinal fluid which can hamper the bonding process.

Steps: In these, enamel is selectively etched with 37% phosphoric acid (taking care not to etch dentin). After washing and drying the tooth, primer and adhesive are applied separately or in combination. This results in micromechanical interaction of dentin and bonding system without exposure of collagen fibrils. For example, Prime and Bond.

Smear Layer Removing Dentin Adhesives

These bonding agents completely remove the smear layer employing total etch concept. They work on the principle of hybrid layer and resin tags.

Steps: In these, enamel and dentin are etched simultaneously using an acid (preferably 37% phosphoric acid). After washing and drying the tooth surface, primer and bonding agent are applied either separately or in combination. For example:

- Scotch bond multipurpose
- Gluma.

Smear Layer Dissolving Adhesives

These agents partly demineralize the smear layer and the superficial dentin surface without removing the remnants of smear layer or the smear plugs. They make use of acidic primers also termed as self etch primers or self etch adhesives which provides simultaneous conditioning and priming of both enamel and dentin.

After this, adhesive is applied without washing the tooth surface.

The basis for use of these systems is to condition the dentin and to simultaneously penetrate to the depth of demineralized dentin with monomers which can be polymerized. For example:

- Self etch primer – Adper prompt
- Self etch adhesive – Prompt – L – pop

GLASS IONOMER BASED ADHESIVE SYSTEM

This is a new revolution in the adhesive dentistry where adhesive agents are based on resin modified glass ionomer technology. Glass ionomer based adhesives are resin diluted versions of resin modified glass ionomers

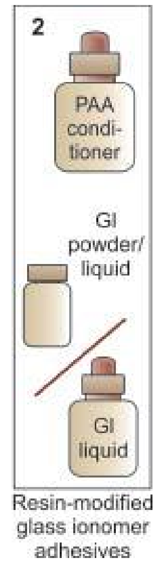


Fig. 16.30: Glass ionomer based adhesives

where bonding occurs by interdiffusion of resin which forms the hybrid layer and then the chemical bonding takes place between tooth and the glass ionomer **(Fig. 16.30).**

Steps

Here both enamel and dentin are conditioned using polyacrylic acid and washed. Polyacrylic acid conditions the tooth surface by removing the smear layer and exposing the smear plugs. After this, adhesive is applied and light cured. For example, Fuji bond LC.

Advantages

- Easy and simple application
- Anticariogenicity because of fluoride release

- Dual bonding mechanism
  a. Micromechanical
  b. Chemical
- Adhesive filled with viscous particles, thus act as shock absorber.

Disadvantages

- Adequate bonding requires smear layer removal.
- Coarse particles present in formulation may result in white lines around restoration.
- Long term clinical research not present.

FAILURE OF DENTIN BONDING (FIG. 16.31)

Reasons for failure of dentin bonding

Dentin can show poor bonding because of following reasons:
- Variable structure of dentin
- Contamination of dentin with sulcular fluid or saliva
- Structural changes of dentin close to pulp make it difficult to bond
- Thickening of bonding agent because of evaporation of solvent. This reduces the penetration of bonding agent.
- Contamination of tooth surface by lubricants used in handpieces.
- Any contact of tooth surface with blood, can result in decrease in bond strength.

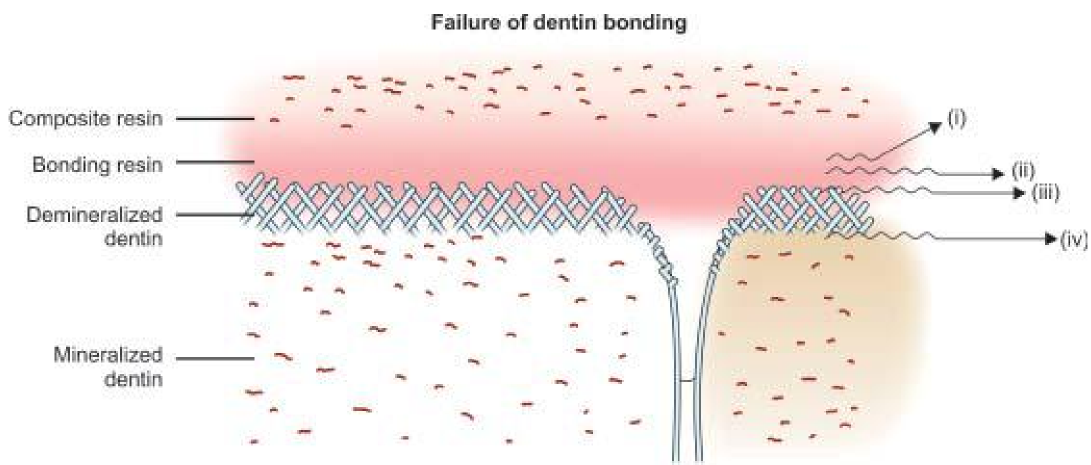


Fig. 16.31: Failure of composite adhesive and tooth joint can occur between: (i) mineralized and dimineralized dentin; (ii) bonding agent and dentin; (iii) bonding agent; (iv) composite and bonding agent