Fundamental Concepts of Enamel and Dentine Adhesion

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Adhesion Meanings

- Latin word adhaerere (to stick to)
- Adhesion / bonding -- The joining together of two objects using glue or cement
Termonologies

**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

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

**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.
ADHERENT: Resin Composite, Ceramic, Acrylic

ADHESIVE: Adhesive resin, Silane primer, tin plating

ADHEREND: Enamel, dentine, Alloy, ceramic
Mechanisms of Adhesion

- Mechanical
- Chemical/Adsorption
- Diffusion
- Electrostatic
Bonding using surface irregularities

Micromechanical

Macromechanical

Amalgam, composite, ceramics
Chemical Adhesion

- Involves chemical bonds between the materials being joined

- Primary Forces
  - Ionic
  - Covalent

- Secondary forces
  - Hydrogen bonds
  - Dipole interaction
  - Van der Waals
Diffusion Adhesion

- Interlocking between mobile molecules
- Diffusion of polymer chain ends
Electrostatic Adhesion

- An electric double layer at the interface of a metal with a polymer that is part of the total bonding mechanism
Advantages of Adhesive Restorative Technique

- Expanded range of clinical treatments
- Conservation of tooth structure
- Reduction in microleakage
- Enhanced retention of restorations
- Reinforcement of tooth structure
- Repair of restorations
- Reduction in dentine hypersensitivity
Enamel Adhesion
FIG. 5-8  Composition of enamel and dentin by volume percentage.
Enamel Composition

- 88% by weight inorganic component (hydroxyapatite)
- Crystalline structure is fairly constant at different levels
- Minor organic components
- Water (very low percentage)
Etching of enamel with 37% orthophosphoric acid for 15 -- 60 secs produce micropores

30 – 40% phosphoric acid removes about 10mm of the enamel surface

A low viscosity liquid polymer (bonding resin) applied and flows into microscopic irregularities and set, producing RESIN TAGS

Then layers of restorative materials bond to this bonding resin
Adhesion to Enamel

- Bond strength → 20 --50 mPa
- Simple and strong adhesion
Enamel etching pattern

– Type I: dissolution of prism cores without involving the periphery

– Type II: opposite of type I

– Type III: less distinct type.
Enamel etching pattern

FIG 11-27  Etching patterns of tooth enamel. A, Etching pattern characterized by removal of prism core. B, Etching pattern showing loss of prism periphery. C, Both etching patterns are evident. (B and C, Courtesy Dr. Leon Silverstone.)
Bonding systems are primarily unfilled acrylic monomer mixtures, similar to the matrix of the composite, that are preplaced onto etched tooth surfaces to form a 1- to 5-μm film.

It micromechanically interlocks with the etched surfaces, seals the walls of the preparation, and copolymerizes with the composite restorative material that fills the tooth preparation.
Adhesion to Enamel

Etch & Wash

Bonding Resin

Restoration
Dentine Adhesion
A typical cavity preparation has more dentine available for bonding than enamel.

- Inorganic 50%
- Organic 25%
- Water 25%
Bonding to Dentine: Challenges

- Only peritubular dentin is etched
- Odontoblast processes in dentinal tubule and fluid
- 45000 tubules/mm² near pulp (22% area). Average size is 0.63um
- 20000 tubules/mm² near DEJ (1% area). Average size is 2.37
- Smear layer (hydroxyapatite and altered denatured dentinal protein)
Problems to overcome include

- Presence of smear layer
- Mineralised tissue
- Dentine tubular fluid and moisture
- Physico-chemical conditions (temperature, oxygen, atmospheric pressure)
- Outward flow of dentinal fluid via pulpal pressure
- Presence of a collagen matrix (not easy to bond to collagen)
- Dentine pain- post-op sensitivity
Dentinal Tubules Distribution & Mineralized Tissue

- Reparative Dentine
- Multizoned Carious Lesion
- Outer Occlusal Dentine
- Inner Occlusal Dentine
- Reactive Dentine (erosion, abrasion)
- Physiologic Dentine (aging, wear)
- Many Occluded Tubules
Dentine Bonding System

Etch & Wash

Bonding Resin

Restoration
Dentine Bonding System

Does not work

Etch & Wash
Bonding Resin
Restoration
Evolution of Dentin Bonding Agents
First generation dentin bonding agent (DBA)

- Surface active comonomer N-Phenyl glycine glycidyl methacrylate **NPG GMA**.

- Comonomer could chelate with calcium on the tooth surface to generate water resistant chemical bonds of resin to dentin Ca.

- Bond with smear layer

- No concept of dentine conditioning

- 2-3 Mpa strength
First generation bonding agents ignored the smear layer. The bonding occurred because of deep penetration of resin tags into open dentinal tubules.
Second generation DBA

- **Phosphate ester material** (phenyl P and Hydroxyethyl methacrylate (HEMA) in ethanol)

- Mechanism was polar interaction between negatively charged PO$_4$ group in resin and positively charged Ca ion in the smear layer

- Relied on adhesion to smear layer

- No concept of dentine conditioning

- 1-5 MPA strength
Third generation DBA

- Employed the concept of dentine priming and conditioning
- Involves modification of smear layer
- Three steps application
  - Etching + Primer+ Bonding Resin
- High bond strength
Third generation DBA

- Hydrophobic nature of resin didn’t allow strong bond after acid etching of dentin.

- Phosphate based ester material contained HEMA and MDP(10 methacryloyloxy-decamethylene-phosphoric acid) long hydrophobic chain & a short hydrophilic component

- It involved modification of smear layer to allow penetration of acidic monomer Phenyl P.

- Modification of smear layer was done by use of citric acid or maleic acid(2.5%)
Third generation bonding agents involved alteration removal of smear layer by conditioning and priming before bonding.
Fourth generation DBA: Total etch concept

- An acid etching gel that is rinsed off

- A solution of primers that are reactive hydrophilic monomers in ethanol, acetone, and/or water

- An unfilled or filled fluid bonding agent. The latter generally contains hydrophobic monomers such as Bis-GMA, frequently combined with hydrophilic molecules such as HEMA
Components of Fourth Generation Dentin Bonding Agents

3 step
Etchant
Fourth generation

Primer
Bonding resin
Fourth generation DBA

- **Etchant**
  - Inorganic acid (e.g., 30-40% orthophosphoric, 2.5% nitric)
  - Demineralises enamel surface
  - Dissolves smear layer
  - Demineralises dentine
Primer

- Actual adhesion promoter, initiates hybrid layer formation
- Contains hydrophilic monomers (eg; HEMA), organic solvent (eg; acetone or alcohol) and water
- Solvents displace water in dentine and allow monomers to permeate the demineralised intertubular dentine, peritubular dentine and the tubules themselves
- The hydrophobic end of HEMA allows chemical compatibility with the supralayer of adhesive resin applied
- The hydrophilic end of HEMA is compatible with the dentinal moisture
Primers are bonding-promoters e.g HEMA&TEGDMA

They are essentially composed of active bi-functional hydrophilic/hydrophobic group of monomer molecules [in water, organic solvents such as ethanol or acetone or a combination them]

Bifunctional gp The hydrophilic part increases substrate surface wettability and permeability enhance resin diffusion into de-mineralized dentin.

The hydrophobic part penetrates inside the created pores where it polymerizes forming retentive tags inside, and co-polymerizes with the applied bonding agent 26
FIFTH generation

- Adding Primer to the bonding agent DBA
- Also called total etch system or single bottle system
- Highest bond strengths in range of 25-30 MPA
3 step
Fourth generation

2 step
Fifth generation

Etchant
Adhesive resin
Primer
Etchant
Adhesive + Primer
Sixth generation (Two steps EP+B)

- Combining etching, priming together
- Called as self etch approach.
- Use of acidic primer a (phosphoric acid ester monomers that performs two functions etching and priming)
- No need of rinsing
- Good dentin bonding but poorer enamel bonding
- Smear layer is still there
Sixth Generation

Etchant+ Primer

Bonding Resin
Seventh Generation: All in one

- One bottle, No mixing at all
- One step, all in one (E+P+B)
- Multiple coats required
- Uncured ionic monomers
- (organophosphates & carboxylates)

Etchant+ Primer+ Bonding Resin
<table>
<thead>
<tr>
<th>Generation</th>
<th>No. of steps</th>
<th>Steps description</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>2</td>
<td>Etch enamel + Apply adhesive</td>
</tr>
<tr>
<td>Second</td>
<td>2</td>
<td>Etch enamel + Apply adhesive</td>
</tr>
<tr>
<td>Third</td>
<td>3</td>
<td>Etch enamel + Apply primer + Apply bonding agent</td>
</tr>
<tr>
<td>Fourth</td>
<td>3</td>
<td>Total etch + Apply primer + Apply bonding agent</td>
</tr>
<tr>
<td>Fifth</td>
<td>2</td>
<td>Total etch + Apply bonding agent</td>
</tr>
<tr>
<td>Sixth</td>
<td>2</td>
<td>Apply self etch adhesive</td>
</tr>
<tr>
<td>Seventh</td>
<td>1</td>
<td>Apply self etch adhesive</td>
</tr>
</tbody>
</table>
Smear Layer

- A layer of dentine, enamel shavings, organic matter, bacteria, blood products, crevicular fluid and saliva which is formed during cavity preparation.

- Bond strength to tooth structure 2-3 Mpa

- Thickness 0.5 – 5 micron

- Reduce dentine permeability 86%

- Can be altered or removed because it is not a very stable adhesion interface
Smear Layer

Dentin

Dentinal tubule

Smear layer 1–2 µm

Smear plug 1–5 µm
Components of Smear Layer

- **Organic**
  - Heated coagulated proteins
  - Necrotic or vital pulp
  - Microorganisms
  - Odontoblastic processes
  - Saliva
  - Blood cells

- **Inorganic:**
  - Tooth structure and non specific inorganic contaminants
Etchant

- Demineralises enamel surface
- Dissolves smear layer
- Demineralises dentine and exposes intertubular and peritubular collagen
- Opens the tubules
- Decrease surface free energy
Types of Acid use

- Citric acid
- Nitric acid
- Oxalic acid
- Acetic acid
- Maleic acid (10%)
- Polyacrylic acid (10%)
- Phosphoric acid. Most used (quick).
Phosphoric acid:

- (PH=1.0)
- Removes about 10 microns of the tooth surface and creates micro-porous layer from 5 to 50 microns
- Liquid, gel or aqueous
- Hypertonic, Osmotically draw fluid from the dentin toward the surface.
- Concentration 30% to 40%.
- Time: 15s to 60s.
Un-etched enamel

Etched enamel
Unetched and Etched Dentine
Primers

- Adhesion-promoting agents

- Consist of:
  - Bi-functional molecules (Hydrophobic with & Hydrophilic groups) (2-HEMA, PENTA)
  - Dissolved in solvents (acetone, ethanol, and/or water)
Objective:

- Envelops the external surface of collagen fibrils
- Re-establishes surface free energy to levels compatible with a more hydrophobic restorative material
Bonding agent

- Bonding agent = adhesive resin

- Primarily consists of
  - Hydrophobic monomers (bis-GMA, UDMA)
  - Viscosity regulator (TEG-DMA)
  - Small percentage of hydrophilic monomer (HEMA)

- Objective:
  - Co-polymerizes with primer molecules
  - Penetrate and polymerizes into the interfibrillar spaces to serve as a structural backbone to hybrid layer
  - It can be light or /and autocuring.
Etching + Priming + Bonding

+ Rinsing
Self Etching Primer + Bonding
Hybrid layer (zone)

- It is a zone in which resin of the adhesive system micromechanically interlocks with dentinal collagen.
- About 0.1 to 5µm deep.
Zones of Hybrid Layer

- Top zone (denature collagen smear gel)
- Midzone (cross-banded collagen fibrils)
- Base layer (resin-enveloped hydroxyapatite crystal)
- Nakabayashi 1982.

- Tubule wall hybridization: Extension of hybrid layer into the tubule orifice.
Zones of Hybrid Layer

- Etched dentin with collagen fibers
- Hybrid Layer
- Dentin Adhesive
- Penetration of the adhesive into dentin
Moist / wet vs Drying Bonding

FIG 5-22 Collapse of etched dentin by air-drying.
Dry vs wet bonding

Dry

Summit et al, 2001

Wet
Moist / wet Bonding
Moist / wet vs Drying Bonding

- **Wet dentin**
  - Areas from where minerals are removed are filled with water
  - Collagen expanded
  - Spaces for resin infiltration are also preserved

- **Dry dentin**
  - Collagen collapse
  - Decrease of the volume of the collagen network to approximately one third of its original volume
  - Additional hydrogen bonds will formed between collagen molecules.
Microleakage

- The clinically undetectable passage of bacteria, bacterial products, fluids, molecules or ions from the oral environment along the gap present b/w cavity walls and restoration

- Effects of Micro leakage
  - Marginal discoloration
  - Post–op sensitivity
  - Secondary caries
  - Pulpal irritation
Nanoleakage

- Small porosities in the hybrid layer or at the transition between the hybrid layer and the mineralized dentine.