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Principles of Adhesion to Tooth Structure

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Abstract: Adhesion or bonding refers to the forces or energies between atoms or molecules at an interface that hold two phases together. Adherends are the surface or substrate that is adhered. While, Adhesive/adherent is the material that can join substances together, resist separation and transmit loads across the bond. This article highlights the concept of adhesion, wettabiltity, factors affecting strength of the adhesive junction, then it focuses on the adhesion in dentistry, factors affecting bonding to tooth structure, Composition of dental adhesive Systems, Classification of dental adhesives and finally, degradation of the adhesive interface.

Keywords: *adhesion, dental adhesive, bonding to tooth structure, etch and rinse, self-etch and wet bonding.*

I. Adhesion

Adhesion or bonding refers to the forces or energies between atoms or molecules at an interface that hold two phases together. Adherends are the surface or substrate that is adhered. While, Adhesive/adherent is the material that can join substances together, resist separation and transmit loads across the bond.(1)

II. Adhesion mechanisms

Mechanical adhesion: It occurs when the solidified adhesive interlocks micro -mechanically with roughness and irregularities of the surface of the adherend (substrate).

Physical adhesion

- **Van der Waals interactions**: Attraction between opposite charges on ions and dipoles.
- **Dispersion forces**: Interaction of induced dipoles
- **Hydrogen bond:** It is a particularly strong bond and can be included among physical forces.(1)

Chemical adhesion: It refers to the forces or energies between atoms or molecules at an interface that holds two phases together. This can be formed by either Adsorption or Diffusion.

- **Adsorption mechanism**: It occurs when chemical bonds develop between the adhesive and adherend including ionic and covalent bonds.

Diffusion mechanism: It occurs when polymers from each side of an interface could cross over and react with molecules on the other side to allow disappearance of the interface.

Ideal requirement of adhesion is chemical affinity between the adhesive and the substrate.

III. Wettability

In order for the adhesive to create a bond between two materials, it must make intimate contact with the surfaces of the substrates such that no air voids (which would weaken the bond) are formed. The ability of an adhesive to contact a substrate depends on the ***wettability*** of the adhesive on that particular substrate. *Good wetting* is the ability to cover the substrate completely, so that the maximum benefit is obtained from whichever adhesive mechanism is activated.(2)

Wetting ability of an adhesive depends on 2 main driving forces.

- Forces that tend to spread the adhesive over the substrate; the surface energy of the substrate and surface tension of the adhesive.
- Resistance to spreading that depends on the viscosity of the adhesive, the surface irregularities and the presence of contaminants.

Surface energy & surface tension

In the bulk of a solid or a liquid, the molecules are subjected to attractive forces in all directions, such that the molecule is in dynamic equilibrium with its surrounding molecules. At the surface, this delicate balance is destroyed, resulting in a net inward attraction directed towards the large number of molecules in the mass of the material. It is this inward force that gives rise to the **surface energy** of a material. In liquids, the surface energy is known as the **surface tension**.

By increasing surface energy of a solid, wettability increases.

One of the effects of surface tension is the tendency for liquids to take up a spherical shape in preference to any other. This arises because a sphere has the minimum surface area for a given volume of liquid, allowing the total energy stored in the liquid to be a minimum. By increasing surface tension of a liquid, wettability decreases.

Contact angle

When a solid and a liquid make contact, the angle between the liquid surface and the solid surface is known as the *contact angle,* and is dependent on the surface tension of the liquid and the surface energy of the solid. For perfect wetting, which is the ideal situation for adhesion to occur, this angle should be 0°. In this case, the surface is completely covered with the adhesive and the maximum bond strength can be achieved.

Viscosity

For an adhesive to be effective, it must be able not only to make intimate contact with the substrate, but also to spread easily on it, Too high a viscosity is undesirable, as it prevents the fluid from flowing readily over the surface of the solid and penetrating into narrow cracks and crevices.

Surface roughness

The measurement of contact angles assumes that the surface of the substrate is perfectly smooth. In reality, the surface may be quite rough at a microscopic level. This roughness has the advantage of increasing the potential area for bonding, but can also lead to the entrapment of air. Such entrapment will significantly reduce the effective bonding area and result in a weak bond. Cracks and crevices constitute surface irregularities and the adhesive must be able to flow into them.

An irregular surface has a higher surface area than a smooth surface, so more chemical bonds can be created. If the irregularities are of a particular favorable morphology, such that undercuts are present at the microscopic level, the bond can be enhanced by the process of micromechanical interlocking.(2)

IV. Factors affecting the strength of the adhesive junction

- The thickness of the adhesive film: the thinner the adhesive film, the stronger the adhesive junction is.
- The degree of wettability of the adhesive to the adherend.
- Induced stresses:
  - Stresses due to setting contraction of the adhesive that results in creation of stresses at the interface. The less the contraction of the adhesive during setting the less will be the stresses and the stronger will be the joint.
  - Stresses due to large difference between the coefficient of thermal expansion and contraction between the adhesive and adherend. Close matching is required to minimize these thermal stresses.
- Type of bond. Ideal requirement of adhesion is chemical affinity between the adhesive and the substrate.
- Cleanliness of the surface is necessary to provide intimate contact which is necessary to produce adhesion.

V. Adhesion in Dentistry

Michael Buonocore is considered to be the first person to propose the application of adhesion technology in dentistry. His groundbreaking research in **1955** demonstrated for the first time that acid-etching of enamel could provide a surface suitable for bonding with resins. (3)

The functions of dental adhesives is to promote conservation of tooth structure and enable minimally invasive dentistry, reinforcement of weakened dentin or enamel, reduce marginal staining, reduce microleakag and may also reduce postoperative sensitivity when used properly.

The ultimate goal of a bonded restoration is to attain an intimate adaptation of the restorative material with the dental substrate. This task is difficult to achieve as the bonding process for enamel is different from that for dentin. Dentin has different composition than enamel, it has higher organic and water content. This humid and organic nature of dentin makes bonding extremely difficult.(4)

1. Bonding to tooth structure

Tooth composition is not homogeneous. Both organic and inorganic components are present in different amounts in dentin as compared with enamel. A material that can adhere to the organic components may not adhere to the inorganic components, and an adhesive that bonds to enamel may not adhere to dentin to the same extent. The instruments used to prepare the tooth for bonding leave a rough surface and debris, which promote air entrapment at the interface, prevent intimate contact between the tooth structure and the adhesive material in addition to dealing with saliva contamination.(5)

The fundamental mechanism of adhesion to tooth structure can be regarded simply as an exchange by which inorganic tooth material (hydroxyapatite) is replaced by synthetic resins. This process involves two parts: removing hydroxapatite to create micropores and infiltration of resin monomers into the micropores and subsequent polymerization. As a result, **resin tags** are formed that micromechanically interlock or interpenetrate with the hard tissue. There may also be chemical interactions with the tooth substrate if monomers having acidic or chelating functional groups are present. (5)

Whenever both enamel and dentin tissues are mechanically cut, especially with a rotary instrument, a layer of adherent grinding debris and organic film known as a **smear layer** is left on their surfaces and prevents strong bonding. Different quantities and qualities of smear layer are produced by the various cutting and instrumentation techniques. In dentin, the smear layer becomes burnished into the underlying dentinal tubules and lowers dentin permeability, which is a protective effect. However, it is also a very weak cohesive material and interferes with strong bonding. Therefore, various cleaning or treatment agents and procedures are employed to either remove the smear layer or enhance its **cohesive strength**. Application of acid is used to remove the smear layer from both enamel and dentin. Alternatively, in dentin the smear layer can be left partially in place and modified such that adhesive resins penetrate through it and bond to the intact dentin structures below. (5)

Bonding to enamel:

Composition: Dental enamel is composed of ~96% carbonated apatite, ~3% of water and less than 1% of organic matrix by weight. The basic building block of enamel is the enamel rod.

Acid etching: Phosphoric acid is the most widely used etchant for bonding to enamel. Depending on the concentration, phosphoric acid removes the smear layer and about 10 microns of enamel to expose prisms of enamel rods to create a honeycomb-like, high energy retentive surface.

Bonding agent: The increased surface energy ensures that resin monomers will readily wet the surface, infiltrate into the formed micropores aided by capillary action, and polymerize to form resin tags

Bonding to Dentin:

Dentin is a dynamic substrate and consequently a difficult substrate for bonding than enamel because of the complexity of the dentin structure.

Composition and challenges:

- Dentin composition is different than that of enamel. dentin consists of 50 vol% (volume percentage) of calcium phosphate mineral (hydroxy-apatite), 30 vol% of organic material (mainly type I collagen), and 20 vol% fluid. Acid etching removes hydroxyapatite almost completely from several microns of sound dentin, exposing a microporous network of collagen suspended in water.
- Dentin is heterogenous. Dentin contains a dense network of tubules that connect the pulp with the dentin-enamel junction. The tubules are lined by a cuff of hypermineralized dentin called **peritubular dentin**. The less-mineralized **intertubular dentin** contains collagen fibrils with the characteristic collagen banding. The intertubular dentin is penetrated by submicron channels, which allow the passage of tubular liquid and fibers between neighboring tubules, forming intertubular anastomoses.
- Movement of fluid present in dentinal tubules from the pulp to the dentin- enamel junction is a result of a slight but constant **pulpal pressure**.

○Dentinal tubules enclose cellular extensions from the odontoblasts and therefore are in **direct communication** with the pulp.

○When tooth structure is prepared with a bur or other instrument, residual organic and inorganic components form a "**smear layer"** of debris on the surface . The smear layer fills the orifices of dentin tubules forming smear plugs and decreases dentin permeability. The composition of the smear layer is basically hydroxyapatite and altered denatured collagen. Submicron porosity of the smear layer still allows for diffusion of dentinal fluid .The removal of the smear layer and smear plugs with acidic solutions may result in an increase of the fluid flow onto the exposed dentin surface. This fluid may interfere with adhesion, because hydrophobic resins do not adhere to hydrophilic substrates even if resin tags are formed in the dentin tubules.

○Dentin is a **dynamic tissue** which shows changes due to aging, caries or operative procedures.

○Several additional factors affect dentin permeability. Besides the use of vasoconstrictors in local anesthetics, which decrease pulpal pressure and fluid flow in the tubules, other factors such as the radius , length of the tubules and the viscosity of dentin fluid.

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

○*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.

The amount of water left in etched dentin is critical. If insufficient water is present, the collagen network will collapse and produce a relatively impermeable layer that prevents resin infiltration and subsequent hybridization. If too much water remains, resin infiltration cannot fully replace the water in the collagen network and, consequently, sets the condition for later leakage into those locations. Therefore, a priming step is required to maintain a hydrated collagen network while removing excess water.

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

○*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). (1, 6)

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. 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. Commonly used primers have HEMA and 4-META monomers, dissolved in organic solvents.

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. 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 or when the organic matrix is denatured. 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. So, it is advisable to have moist dentin for resin-dentin bonding, to achieve successful dentin bonding. (1, 6)

VI. Factors affecting bonding to tooth structure

There are different factors that affect bonding to tooth structure that could be classified into five main groups; tooth related, material related, cavity related, technique related and oral environmental factors.

Tooth related factors including:

- **Surface energy** of enamel and dentin surface as mentioned before. Increased surface energy is required for good adhesion.
- **Capillary attraction**. If there is good wetting, then capillary action will end to draw the material to the surface (irregularity or orifice). keeping in mind that the viscosity must be low enough for the material to penetrate into the defected site.

- **Compositional differences of tooth tissues**. Tooth composition is heterogenous. Both organic and inorganic components are present in different amounts in dentin & enamel.
- **Presences of smear layer** on surface of prepared enamel and dentin and how to deal with.
- **Contaminants** presence of contaminants that prevents the intimate contact between the tooth structure and adhesive affecting the bond strength negatively.

Material related factors

- **Degradation** of the adhesive junction in the oral fluids (that will be discussed later)
- **Thermal coefficient of expansion** as mentioned before the large difference between the coefficient of thermal expansion and contraction between the adhesive and tooth structure induce thermal stresses that affects the strength of the bond.
- **Modulus of elasticity and transfer of stress at interface.** The adhesive must have modulus of elasticity close to that of tooth structure to avoid stress shielding effect.
- **Dimensional stability** of the material used.

Prepared cavity related factors

All these factors should be considered during cavity preparation to maximize the achieved bond strength:

- Adhesive **cavity design** should be done.
- **Resistance and Retention** required should be estimated and built in preparation.
- All carious tissue should be removed.
- Adequate **finishing**, **debridement** and **toilet** of the cavity is required.

Technique of restoration and skills of the operator factors

o Avoid moisture contamination.
o Use of liner and bases.
o Constituents of temporary restorations.
o Post-operative and post restorative care.
o C-factor.

N.B: An important clinical consideration during the application of the adhesive to the prepared tooth structure is the **configuration factor (C-factor)**. The C-factor is the ratio of bonded surfaces to the unbonded or free surfaces in a tooth preparation. The higher the C-factor, the greater is the potential for bond disruption from polymerization effects (stresses are induced at the adhesive junction due to the polymerization shrinkage of the adhesive during setting, while the tooth structure is rigid).

Oral environmental factors

o Occlusal loads.
o Chemical degradation.
Oral microorganisms.
o Humidity.
o Chewing habits.

All these factors have negative impact on the strength of the adhesive junction and its durability.

VII. Composition of dental adhesive System

☐ Etchant:

In etch and rinse technique the etchant used is 30% - 40% phosphoric acid gel (pH = 0.1–0.4). In enamel phosphoric acid etching removes the smear layer and approximately ≅ 10 μm of the enamel surface, creating a porous area with increased surface energy and wettability. This enables fluid resin infiltration, forming resin tags.

However, etching dentin surfaces with phosphoric acid leads to a complete removal of the smear layer and demineralizes the intertubular dentin, leaving a 3D microporous mesh of exposed collagen fibrils, devoid of hydroxyapatite making chemical bonding with is unlikely. Hence, the primary bonding mechanism of etch & rinse adhesives to dentin depends on infiltration of resin within the exposed collagen fibril scaffold. However, complete infiltration of monomers into the wet and demineralized dentin is not consistently achieved, leaving incompletely infiltrated zones along the bottom of the hybrid layer in the form of “nanoleakage” phenomena. (12)

Even after the air drying , dehydration of the demineralized dentin leads to the collapse of the exposed collagen mesh, reducing the spaces between the fibrils and preventing them from acting as channels through which monomers may penetrate and spread.

In self-etch adhesive, the etchant is typically an acidic monomer that also serves as the primer so the previous problem does not exist.

☐ Primer:

The main aim of the priming step is to alter the hydrophilic dentin surface into a hydrophobic phase. The primers, adhesion promoting agents, contain amphipathic monomers dissolved in organic solvents. These monomers have hydrophilic properties with affinity for the collagen fibrils and hydrophobic properties to co-polymerize with the adhesive resin. The (HEMA) monomer is the most frequently incorporated in primers. However, the incorporation of HEMA to adhesive–resin makes dental adhesives too hydrophilic and thus more susceptible to hydrolysis.

Self-etch adhesive systems utilize primers that are acidic monomers. Examples of acidic functional resin monomers are (10-MDP). Overall, 10- MDP is the most popular and highly stable acidic monomer; its stability is attributed to the long carbonyl chain (spacer) between the functional and the polymerizable groups in the monomer structure. Additionally, the phosphate functional group is capable of forming strong ionic bonds with hydroxyapatite, due to the low solubility of the resulting calcium salts. (13)

☐ **Resin components:**

In order to assure a good covalent bond between the adhesive and resin composite, dental adhesives contain resin monomers that are similar to those in resin composite. They act as a backbone providing structural continuity and thus mechanical properties such as strength. Monomers are the key constituents of adhesives. Two kinds of monomers can be distinguished:

- *Cross-linkers hydrophobic monomers* (have two polymerizable groups) which is responsible for its biomechanical properties and co-polymerization with the restorative material as (BisGMA).
- *Functional hydrophilic monomers* (commonly have only one polymerizable group) used for different actions, such as increasing the wettability (e.g. HEMA); provide anti-bacterial properties (e.g. MDPB & 10-MDB).(14)

☐ **Initiator systems:**

Adhesive systems should be cured before the application of the composite, to obtain an optimal degree of conversion, thus good mechanical strength of the adhesive layer.

- **Photo-initiators:** Many compounds can dissociate into free radicals upon absorption of light energy, such as camphorquinone (**CQ**), 1-phenyl-1,2 propanedione (**PPD**) both are hydrophobic. so, may be subjected to phase separation resulting in poor polymerization of the hydrophilic part of the adhesive systems. The use of alternative photoinitiator systems 2-hydroxy-3-(3,4dimethyl-9-oxo-9H-thioxanthen-2-yloxy)-N,N,N-trimethyl-1 propanaminium chloride (**QTX**). The QTX is a water soluble photoinitiator, that improve the polymerization of the more hydrophilic components of the adhesive resin. However, it has very short absorption peak, so need special LED light curing unit.
- **Chemical-initiators:** The use of chemical initiators is usually restricted to cements and resin that cannot rely on light curing for polymerization. The most common initiator in self-curing resins is benzoyl peroxide (**BPO**) in conjunction with co-initiator **tertiary amine**. (14)

☐ **Inhibitors:**

Inhibitors added to dental resins are actually **antioxidants** that are able to scavenge free radicals originating from prematurely reacted initiators. The most frequently used inhibitors in adhesives are butylated hydroxytoluene.

☐ **Fillers:**

Fillers are added to modify the strength and viscosity of adhesives. Depending on their chemical composition, fillers can also provide **fluoride release** and **radioopacity**.

P.S., particle size affects penetration ability.

☐ **Modifiers:**

Manufacturers sometimes add specific ingredients such as: glutaraldehyde, which have desensitizing effect results from denaturation of collagen in dentin and the occlusion of dentinal tubules, in addition to strong antibacterial activity.

Methacryloyloxydodecylpyridinium bromide (MDPB) monomer with antibacterial effect, N-methacryloyl-5-aminosalicylic acid (5-NMSA) monomer has a salicyl group that is intended to chelate with calcium in order to obtain a desensitizing

☐ **Solvent:**

The addition of solvents to resin is essential. The wet nature of dentine only allows good wetting when a hydrophilic bonding is applied. Their main function is to promote good penetration of the monomers in the collagen network of the demineralized dentin, thus improve the diffusion ability of resin.

- **Water:** Water-containing adhesives are capable of expanding the collapsed and shrunken collagen network. Water takes a longer time to evaporate when compared to alcohol.
- **Ethanol:** Its higher vapor pressure compared to water allows faster evaporation by air-drying thus added to water.
- **Acetone:** Its high vapor pressure, which is about **four times** as high as that of ethanol. However, its high volatity reduces shelf life of acetone-containing adhesives, by rapid evaporation of the solvent.

Wet bonding technique

Solubility parameter for hydrogen bonding forces (δh) is used to predict how any solvent or adhesive resin can re-expand a collapsed dried, acid-etched dentin. To re-expand matrices, a solvent or resin monomer blends must have hydrogen bonding force higher than 14.8 $(Jcm^{3})^{1/2}$. Ethanol ($\delta h = 20.0$ $[Jcm^{3}]^{1/2}$) and water ($\delta h = 40.4$ $[Jcm^{3}]^{1/2}$) are successful in breaking interpeptide hydrogen bonds allowing the matrix to re-expand. (15)

Traditional **water-wet-bonding** technique is used to improve initial bond strength of etch-and-rinse adhesives. Water is an excellent solvent to re-expand collapsed demineralized dentin matrices prior to resin infiltration. However, excess water often causes **suboptimal polymerization** of infiltrated resin monomers. Moreover, water is not a proper solvent for resin monomers, as their miscibility is limited in the water, resulting in **phase separations** of hydrophobic resins as Bis-GMA. Resulting in poor quality hybrid layer that is quite susceptible to biodegradation over time in a harsh oral environment.

Ethanol wet-bonding enhances resin infiltration promoting higher quality hybrid layers in comparison with conventional water wet-bonding. The crucial aim of ethanol wet-bonding is to infiltrate the interfibrillar spaces and dentinal tubules with hydrophobic dimethacrylate resins.

Ethanol is used to chemically dehydrate the exposed collagen matrices without causing their collapse. For maximum collagen re-expansion water is added (28-45 vol%) to ethanol without detection of phase separation.

However, remaining solvent within the adhesive layers may impair adhesive polymerization. Therefore, thorough and careful air drying of the adhesive is necessary to remove excess solvent before the light curing of the adhesive. (15)

VIII. **Classification of dental adhesives**

Different classifications have been introduced over the years for adhesives; according to generation, method of etching and the number of bottles involved or the number of individual steps necessary for the entire bonding procedure.

- **According to Chronology**

Dental adhesives can be categorized chronologically into generations. The generation simply refers to when and in what order this type of adhesive was developed by the dental industry, ranging from 1st generation in the 1960s to modern 8th and 9th adhesives. 1st and 2nd generation bonding agents are no longer used. They achieved poor bond strengths and failed to prevent marginal gaps. However, 3rd, 4th, 5th and 6th generation adhesives are popular and offer various advantages depending on the clinical situation and the clinician's personal preferences and experience. (4)

- **According to clinical application steps**

Modern dental adhesives can be classified into two basic types: etch-and-rinse (total etch) and self-etch adhesives. These systems can then be sub-classified based on the number of clinical steps included into: three-step and two-step etch and rinse systems. Self-etch system is classified into two-step and one-step self-etch systems.

- **According to adhesion strategy**

Smear layer removing adhesive systems (etch and rinse approach), smear layer dissolving adhesive systems (self-etch approach) and Glass-ionomer approach self-adhesive‖ due to the ionic interaction of polyalkenoic acid with calcium in hydroxyapatite forming submicron hybiridization.

- **Etch and rinse or total etch approach**
  (Smear layer removing adhesive systems)

The **etch-and-rinse system** has a separate etch-and-rinse step before the priming and bonding steps. The 3-step etch-and-rinse (total-etch system) (using fourth generation adhesives) follows the conventional "etch-rinse-prime-bond" approach. The two step etch-and-rinse system (using fifth-generation adhesives) combines the primer and the bonding agent into one application. (4)

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

The advantage of this system is that, it provides the highest enamel bond strength. However, this technique results in low dentin bond strength, it is technique sensitive, and results in post-operative sensitivity and nanoleakage. While, with sclerotic dentin, etch and rinse system is better, because, the hyperminerialization of dentin and reduced size of dentinal tubules. (4)

- **Self-etch approach (Smear layer dissolving adhesive systems)**

The **self-etch adhesive system** eliminates the rinsing phase after etching by using non-rinse acidic monomers to etch and prime dentin simultaneously. The two-step self-etch system (involving sixth generation adhesives) uses **hydrophilic acidic monomers** as self-etch primers in the initial step and an **adhesive hydrophobic resin** in the second step. The one-step self-etch system (using seventh generation adhesives, also known as all-in-one adhesives) combines the (self-etch) acidic primer with the adhesive resin in one application step. This allows for simultaneous infiltration of adhesive resin to the depth of demineralization, which decreases the discrepancy between the depth of demineralization and the depth of resin infiltration resulted with etch and rinse system. (4)

These agents partially 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 provide 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.

As one-component self-etch bonding systems mix hydrophilic and hydrophobic agents in the same bottle, they are generally **not as acidic as** other adhesives and can therefore **bond poorly** to enamel and sclerotic dentin. In addition, a difficulty with formulating one-bottle systems is **maintaining stability** with a mixture of components and avoid the phase sepration. In order to solve such a problem, one-step self-etch adhesive systems are supplied as two bottles or unit dose that require mixing just before application.

The etching aggressiveness of self-etch adhesive systems can also be classified into:

- **Strong (pH<1)**: At enamel, “strong” self-etching shows good bonding performance. While, at dentin, “strong self-etching” dissolves nearly all the smear layer but does not remove the dissolved calcium and phosphates ions. These loosely embedded calcium phosphates are hydrolytically unstable, thereby weakening the interfacial integrity on the long-term.
- **Intermediately strong (pH≈1.5):** It has typically a hybrid layer with demineralized top layer and partially demineralized base.
- **Mild (pH≈2):** partially dissolves the smear layer, forming a thin hybrid layer. It has a great advantage of leaving significant amount of hydroxyapatite- crystals around collagen fibrils, which may form chemical bond with carboxylic or phosphate groups of functional monomers. Furthermore, less amount of MMPs will be released form collagen.
- **Ultra-mild (pH≥2.5):** can only expose superficial dentin collagen, producing a nanometer interaction zone.

Advantages of self-etch adhesive:

1. Improve technique sensitivity and control the tooth wetness issue.
2. Better protection of collagen fibrils compared to the E&R technique.
3. Less post-operative sensitivity

Limitations of self-etch adhesive:

Chemically cured composite resins that use tertiary amine as activator do not bond well with self-etch adhesives. This is because the acidic monomers in the self-etch adhesives deactivate the more basic tertiary amines. This problem is overcomed by an additional bottle of chemical co-initiator containing sodium benzene sulphinate.

- **Universal "multi-mode" adhesive systems**

These products are known as multi-mode″ as it can be used as: self-etch (SE) adhesives (one step), etch-and-rinse (E&R) adhesives (two step) and in selective enamel etching.

Most of the formulations of universal adhesives include a chemical bonding capability due to presence of functional monomers that chemically bond to hydroxyapatite, which has been proven to be important for the stabilization of the bond over time.

Among the currently used functional monomers, 10-methacryloy- loxydecyl dihydrogen phosphate (10-MDP) demonstrated a very effective and durable bonding to dentin. (7)

10-MDP can ionically bond to calcium (Ca++) ions and form stable MDP-Ca salts. These salt deposits at the adhesive interface form self-assembled nano layers. When the MDP-containing adhesive is applied onto the dentin covered with a smear layer, the surface is partially demineralized up to a nanometer in depth. Ca++ ions released by the partial dissolution of dentin diffuse within the hybrid layer and form MDP-Ca self-assembled nano layers.(8)

In vitro studies have shown that the use of a multimode universal adhesive in either the etch and rinse or self-etch application mode did not result in significant difference in dentin bond strength. (9, 10, 11)

Examples: Scotchbond Universal (3M ESPE) & All-Bond Universal (Bisco Dental) (7)

Disadvantages of universal adhesive:

- Universal adhesives cannot infiltrate to the full depth of demineralized dentin created by phosphoric acid in case of E&R strategy.
- The complex formulation with high content of solvents may impair complete solvent volatilization and consequently lead to inferior adhesive polymerization.

IX. Degradation of the adhesive interface

☐ Nano-leakage

Nano-leakage is the presence of porous zones beneath or within the hybrid layer that allows penetration of small molecules. It is created by the discrepancy between dentin demineralization and resin infiltration in etch and rinse adhesive systems. The hybrid layer act as a permeable membrane, allow water movement through the bonded interface that plasticizes the polymer chains as shown in Fig. 1.

Self-etch procedures use acidic adhesive resin monomers to simultaneously demineralize and infiltrate the bonding substrate. Thus, theoretically avoiding incomplete infiltration aiming to minimize nano-leakage.

Simplified one-step self-etching adhesives are highly hydrophilic and form hybrid layers that have been found to behave as permeable membranes after polymerization, permitting water movement throughout the bonded interface. Moreover, the retention of residual water in etched dentin and/or adhesives may result in regions of incomplete polymerization or increased permeability within adhesive resin matrices resulting in nano-leakage.(16)

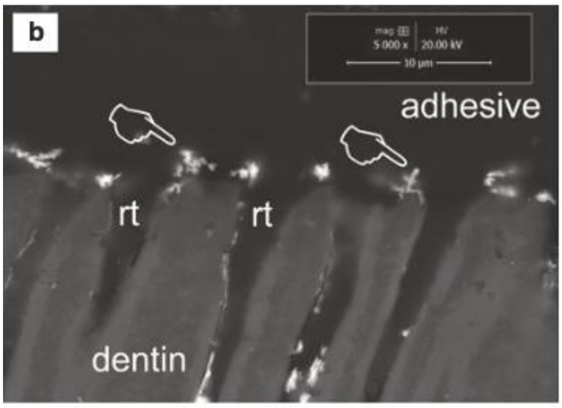

Fig. 1. SEM image of a specimen created with the ethanol wet-bonding technique in dentin pretreated with oxalic acid and submitted to simulated pulpal pressure. Very little nanoleakage can be appreciated within the resin-dentin interface. (14)

☐ Degradation of the Resin Matrix

Most adhesive systems produce very good immediate bond strengths, but the long-term strength is questionable. Adhesive systems are not able to infiltrate completely the demineralized collagen matrix in the acid-etched dentin due to the inability of resin monomers to displace water. This leads to micro- and/or nano-phase separation within the hybrid layer (nano-leakage). These represent the **critical sites** where the hydrolytic degradation can occur causing decrease in the durability of the resin-dentin bond.

However, hydrolysis of resin matrices occurs in both self-etch (SE) and etch-and-rinse (ER) adhesives. Moreover, it is related to their **degree of hydrophilicity** and the amount of water sorption within the hybrid layer. Subsequent to water sorption, these materials are subject to hydrolytic effect, which influences their mechanical properties, dimensional stability and biocompatibility.

Polymer chains within light-cured adhesives absorb water and undergo volumetric changes such as swelling and physical changes such as plasticization and degradation. Degradation occurs through two main mechanisms: (1) passive hydrolysis and (2) enzymatic reaction.

Dental polymer networks may undergo hydrolytic reactions that cause scission of the polymer chain (breakdown of double covalent bonds).

Saliva contains several **esterases** that may cause esterification of methacrylates. The degree of enzymatic degradation is related to the degree of cure of resin monomers at the resin-dentin interface. Loosely cross-linked resin networks are characterized by the presence of ester groups that may be more susceptible to degradation.

The degradation of the polymer matrix is also related to **the chemical composition** of the adhesive. The higher the amount of hydrophilic monomers, the greater the water sorption and hydrolysis.

It is widely accepted that 3-step ER and 2-step SE adhesive systems can be considered as the ‘gold standard’ in dental adhesion. The reason being that is the placement of a hydrophobic adhesive over a primered dentin that reduces water sorption within the resin-dentin interface. While, adhesive systems with fewer application steps, such as all-in-one SE, 2-step ER and universal adhesives exhibit lower bond strength over time and less predictable clinical results compared to the more complex adhesive protocols. Such simplified adhesives are too hydrophilic and allow water sorption, which leads to more drastic hydrolytic degradation of the resin matrix (14)

- **Enzyme-Mediated Collagen Degradation**

The bulk of the tooth is made of dentin, which is constituted by a **mineral component** of up to 70 vol% calcium-deficient/carbonate-rich hydroxyapatite and 30% of **organic content** (90% collagen fibrils and 10% water-rich non-collagenous proteins (NCPs) such as proteoglycans, glycosaminoglycans, phospholipids and enzymes). The enzymes are mainly endogenous MMPs and cysteine cathepsins (e.g. cathepsin K) proteases bonded to the collagen matrix as inactive enzymes proforms and fossilized within the mineralized dentin.

- When MMPs (e.g. MMP-2, MMP-9) are exposed and **activated during restorative procedures** using acid etchants (ER bonding approaches) or acidic resin monomers (SE bonding approach). Moreover, it has been demonstrated that acidic resin monomers contained in mild SE adhesives can **inhibit tissue inhibitors of metalloproteinases** (TIMPs) thus allow MMPs activation. The optimum pH for MMPs to function is between 7.2 and 7.5.
- Cathepsin K has proteolytic activity that leads to collagen degradation within the hybrid layer. The optimum pH for cathepsin K is around 5.0.

However, there is an agreement in adhesive dentistry that collagen degradation is more evident with ER approaches, as the use of phosphoric acid-etchant demineralizes more dentin compared to other approaches, leaving collagen matrices exposed and making them more susceptible to proteolytic degradation by endogenous enzymes . (17)
While, In SE adhesives etch and resin infiltrate the dental substrate simultaneously preventing complete exposure of collagen fibres and preventing also removal of smear plugs from dentinal tubules. Thus, collagen fibrils remain protected by HAP crystallites and less water sorption from the pulpal chamber. (17)

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