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Bonding of dentistry

A Graduation Project Submitted to the Council of the College of Dentistry at University of Baghdad (Department of conservative), in Partial Fulfillment of the Requirements for the Bachelor Degree in Dental Surgery (B.D.S)

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(وان ليس للإنسان إلا ما سعى ○ وان سعيه سوف

(يرى))

صدق الله العظيم

سورة النجوم آية ٣٩

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I certify that this project entitled "Bonding in dentistry" was prepared by "hala walid hasan" under my supervision at the College of Dentistry / University of Baghdad in partial fulfillment of the graduation requirements for the Bachelor Degree in Dental Surgery.

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DEDICATIONI

dedicate this research project to my father and my mother for their great support even when things were so tough for she constant kept on encouraging me to work extra hard, my friends for support and encouragement throughout my studies and Finally, a special thanks to my supervisor for his guidance and support.

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INTRODUCTION

Improvements in dental adhesive technology have extensively influenced modern restorative dentistry. Nowadays, the surgical approach of 'extension for prevention' proposed by GV Black in 1917 is no longer justifiable, and has been replaced by the concept of 'minimally-invasive dentistry'. This modern approach focuses on the achievement of a more conservative cavity design, basically providing sufficient access for the complete removal of the carious tissue. The subsequent restorative procedure relies on the bonding effectiveness of adhesive materials such as resin composites, which do not require the removal of sound dental structure for additional mechanical retention. Although these restorations tend to fulfil the main requirements of a more conservative and aesthetic treatment, their clinical longevity is still a topical issue, mainly due to the degradation of the adhesive interface over time. Clinically, the main cause of failure of composite fillings is related to the occurrence of marginal leakage, which eventually leads to marginal discolouration, secondary caries, and subsequent loss of retention (Cardoso et al., 2011).

The essential goal of any adhesive restoration is to achieve a tight and long-lasting adaptation of the restorative material to enamel and dentin. The key challenge for new dental adhesives is to be simultaneously effective on two dental substrates of conflicting nature. Some barriers must be overcome to accomplish this objective. While bonding to enamel by micromechanical interlocking of resin tags within the array of microporosities in acid-etched enamel can be reliably achieved and can effectively seal the restoration margins against leakage, bonding effectively and durably to organic and humid dentin is the most puzzling task in adhesive dentistry (Jogo, 2020). In this context, several aspects should be considered with regard to the bond strength and durability of adhesion to dental hard tissues. These include the heterogeneity of tooth structure and composition, the hydrophilicity of the exposed dentine surface, the features of the dental substrate after cavity preparation and the characteristics of the adhesive itself, such as its physicochemical properties and its strategy of interaction with enamel and dentine. The present literature review deals with modern concepts in adhesive dentistry, discussing issues that still challenge the achievement of an optimal interaction between adhesives and dental substrates. For this purpose, a parallel is drawn among the currently available adhesive strategies and

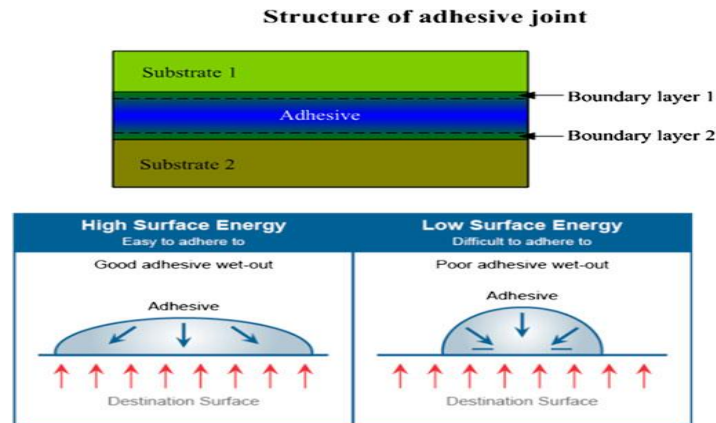
the main factors that interfere with their interaction with enamel and dentine (**Cardoso et al., 2011**).

1.1 Basic Concepts of Adhesion

The American Society for Testing and Materials (specification D907) defines adhesion as "the state in which two surfaces are held together by interfacial forces which may consist of Valence forces or interlocking forces or both. The word adhesion comes from the Latin adhaerere ("to stick to) An adhesive is a material, frequently a viscous fluid that joins two substrates together by solidifying and transferring a load from one surface to the other. Adhesion or adhesive strength is the measure of the load-bearing capacity of an adhesive joint (**Heymann et al., 2013**). Adhesion is the force or the intermolecular attraction that exists between molecules of two unlike substances when placed in intimate contact with each other. The substance added to produce the adhesion is known as the 'adhesive' and the material to which it applied is known as the 'adherend'. An interface is present wherever adhesion exists. Adhesion can be seen between any two phases, e.g. solid, liquid or gas with the exception of two gases where an interface is not present. Most commonly, a solid is the adherend and liquid is the adhesive (**Sikri V K, 2017**).

1.2 Mechanism of Adhesion

To choose the proper adhesive, it is important to understand the mechanism of adhesion and the surface energies of all the substrates, and how well the adhesive will wet out. Surface energy is a physical property of the surface of a material that determines whether an adhesive will make intimate contact and provide a bond. The adhesive interactions between an adhesive and a substrate not only concern the actual area of contact (adhesion zone) of the adhesive and substrate but also concern the state of the adhesive in the vicinity of the surface of the substrate (transition zone). (Fig. 1-1) shows the structure of the adhesive joint and effect of surface energy (**Garg and Oestervemb, 2015**).



structure of the adhesive joint and effect of surface energy

(Fig.1-1) (Garg and Oestervemb, 2015)

Physical means of adhesion involve the:

- 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. (Garg and Oestervemb, 2015)

Chemical means of adhesion involves primary forces that is:

- 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.
- Ionic bond: It involves an actual transfer of electrons from one atom to another. For example, ion exchange adhesion mechanism in GICs.
- Metallic bond: It is the chemical bond characteristics of metals in which mobile electrons are shared among atoms in a usually stable crystalline structure.

(Garg and Oestervemb, 2015).

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

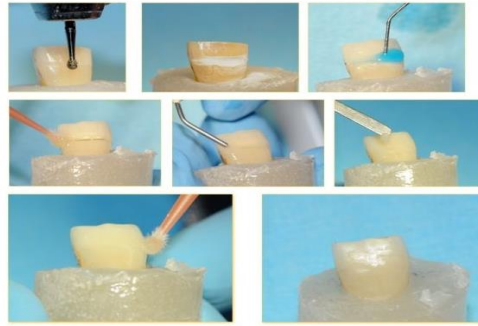
the penetration of resin into enamel and dentin and formation of resin (**Garg and Oestervemb, 2015**).

1.3 Indications of Adhesion:

Adhesive restorative techniques currently are used to accomplish the following:

1. Restore Class I. II. III. IV. V, and VI carious lesions or traumatic defects.
 2. Change the shape and the color of anterior teeth.
 3. Improve retention for porcelain-fused-to-metal or metallic crowns.
 4. Bond all-ceramic restorations.
 5. Seal pits and fissures.
 6. Seal root canals during endodontic therapy.
 7. Seal surgically resected root apices.
 8. Bond orthodontic brackets.
 9. Bond splints for tooth luxations and periodontally involved anterior teeth and conservative tooth-replacement prostheses.
 10. Bond fractured fragments of anterior teeth (Figure 1-2).
 11. Repair existing restorations (such as composite, amalgam) and provide foundations for crowns.
 12. Impregnate enamel and dentin making them less susceptible to caries.
 13. Desensitize noncarious cervical lesions (NCCLs) and exposed root surfaces.
 14. Bond prefabricated fiber, metal, and cast posts.
 15. Reinforce fragile endodontically treated roots internally .
- (Ritter et al., 2019)**

post-reattachment procedure



(Figure 1-2) post reattachment procedure was performed using around bur to create a “double bevel” both on the tooth and on the fragment. The preparation was then filled with composite (flow then regular). (Simone, 2016)

1.4 Important Terms Related to Adhesive Systems

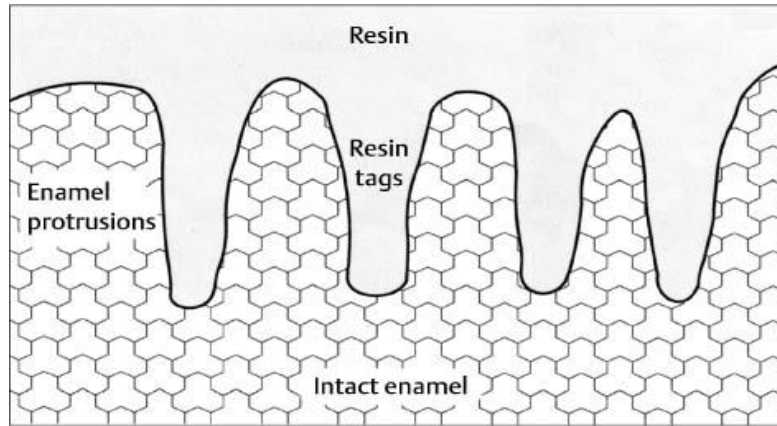
1.4.1 **Hybrid Layer:** An intermediate layer of resin, collagen, and dentin that is produced by acid etching of dentin and infiltration of resin into the conditioned dentin (Anusavice et al., 2013). The main binding mechanism of adhesive restorative materials is based on the formation of the hybrid layer. The hybrid layer was first identified by Nakabayashi in 1982 and expressed as a mixture of demineralized dentin compounds and polymerized adhesive resin at molecular level (Nakabayashi N, 1982).

1.4.2 **Resin Tags:** Oral hard tissues and their environment are complex. However, 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 (fig. 1-3), This process involves two parts:

(1) removing hydroxyapatite to create micropores .

(2) 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 (Garg and Dhillon, 2017).



Resin Tags

(Fig. 1-3) (Garg and Dhillon, 2017).

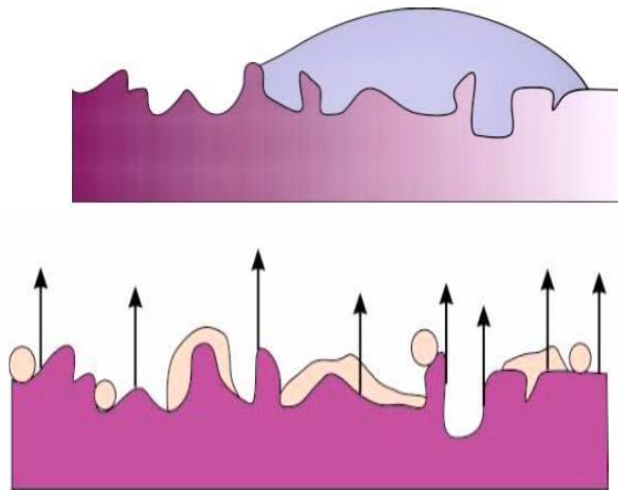
1.0 Factors Affecting Adhesion

The phenomenon of adhesion is dependent upon certain factors. The three factors, surface energy, wetting and contact angle are important determinants of adhesion (Good, 1992).

a. Surface Energy: The energy of a solid on the outer surface is comparatively higher than its interior. Inside the crystal, each atom is equally surrounded by atoms on all sides and the inter-atomic distances are equal, hence the energy is minimal; whereas, towards the periphery, the atoms are not equally distributed. The surface atoms get strongly attracted to each other resulting in surface tension. Because of this energy, substances are attracted to the substrate surface. The adhesive can attach to the adherend either by physical or chemical force. Initially when the two substances are far apart, only physical forces exist between them but as the distance diminishes, chemical forces start becoming effective. Hard solids have specific free surface energy values between 0.00-0.000 ergs/cm². Harder the surface, higher is the surface energy and higher the adhesive properties (Sikri v K, 2017).

b. 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. 1-4). Wetting ability of an adhesive depends upon two factors:

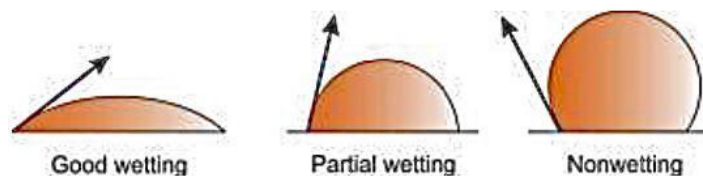
- Cleanliness of the adherend (Fig. 1-5): Cleaner is the surface, greater is the adhesion.
- Surface energy of the adherend: More the surface energy, greater is adhesion.



(Fig. 1-5) A good wetting ensures good adhesion (fig. 1-6) A clean surface increases the adhesion

(Garg and Oestervemb, 2015)

c. Contact angle: 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 (fig. 1-7).



(Fig. 1-7) Lesser is the contact angle, better is the adhesion (Garg and Oestervemb, 2015).

Another requirement for achieving lasting intraoral bonds is hydrolytic stability (resistance to chemical degradation by water). Enamel and dentin are hydrated, hydrophilic, and permeable to water. Even if an enamel or dentin

surface is initially dried before applying an adhesive, inadvertent contamination and diffusion can easily result in water becoming strongly bound to both the hard tissue and the adhesive. Thus, for an adhesive monomer to wet hard tooth tissue as well as form a durable bond in the moist environment of the mouth, it must be both hydrophilic for water compatibility and hydrolytically stable to ensure longevity (Anusavice et al., 2013).

1.6 Tooth As A Substrate For Bonding

The substrate (ex: enamel, dentin) has surface energy and the adhesive (liquid state) (ex: bonding agent) has something called surface tension, If the surface tension of the adhesive is high, it will not spread, therefore to have a good adhesive we need one with low surface tension, therefore it will have a better spread-ability (wettability). In other words, we need a substrate with high surface energy and an adhesive with low surface tension so it can spread easily on the substrate, this is what wettability means (Jeff, 2022) Enamel is easier to bond to because of its structure, it contains almost 90% of inorganic material (calcium, phosphate and hydroxyapatite). It is also more homogeneous (contains less water) than dentin. Based on this we can state that bonding to enamel is stronger because it has high surface energy (caused by the inorganic components) and that adhering to a homogenous substrate is easier, Within the same tissue, nature of the substrate presented for bonding may vary with the location, e.g. enamel etched on its rod ends provide better area for bonding compared to enamel etched on the side of the prisms. Fluoridated enamel has a low surface energy and is more difficult to bond compared to the non-fluoridated enamel, While dentin has 70% inorganic components, 20% organic and 10% water, which makes it harder to bond to, Dentin in its superficial portion allows greater bond strengths than in the deeper portions. This might be because the superficial layer has more of solid dentin and less moisture contamination as compared to deeper portions. In enamel, we can increase the surface energy by phosphoric acid etching which produces irregularities and therefore increases the surface area which will increase the surface energy, it also helps in cleaning the area which is also needed because the pellicle reduces the surface energy of the enamel. Hydroxyapatite has a better surface energy and it accepts adhesion (Jeff, 2022; Sikri V K, 2017) The presence of moisture in dentin is the major hurdle in achieving bonding. The

inherent wetness owes to the outward flow of the dentinal fluid under positive pulpal pressure (**Carvalho et al., 2009**).

In order to obtain a stable and long lasting bond to wet dentin, it is essential that the adhesive displace or be miscible in the fluid in areas where the dentin is most permeable. An important factor that influences the bonding to tooth surface is the presence of smear layer on cut dentin. The smear unit (smear layer + smear plugs) may serve as a contaminant and prevent adequate penetration of the adhesive into the underlying substrate (**Sikri V K, 2017**).

1.7 Properties of Adhesive Systems:

- a. They should be biocompatible and should not damage the pulp tissue of the tooth in particular.
- b. They should be able to connect micromechanically and chemically to hard tissues of teeth (enamel and dentin).
- c. They should prevent post-treatment sensitivity by blocking all/ most of the dentin channel.
- d. Be able to resist the stresses caused by mastication forces and polymerization shrinkage stresses.
- e. They must be resistant to microleakage, prevent secondary caries, and resistant to thermal expansion and thermal shrinkage.
- f. Should be able to apply easily on moist surfaces.
- g. Shelf life should not be short.
- h. Clinical applications should not be difficult and application steps should be reduced and the film thickness should be minimum (less than 20um).

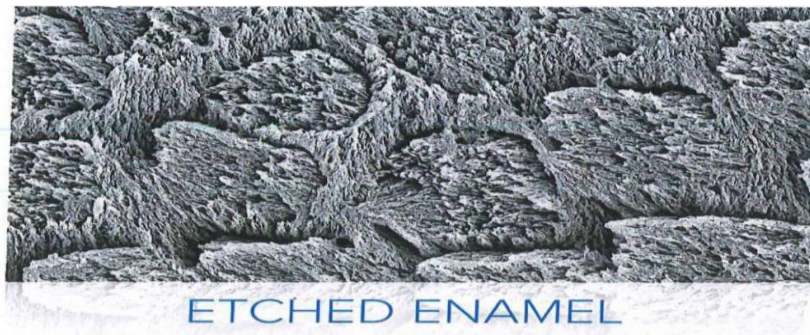
(Van Meerbeek et al., 1998)

1.8 Enamel adhesion

Enamel is the hardest substance in the human body and contains the highest percentage of minerals, 96%, with water and organic material composing the rest. The primary mineral is hydroxyapatite, which is a crystalline calcium phosphate. The basic unit of enamel is called an enamel rod. Measuring 4-8 μm in diameter an enamel rod, formally called an enamel prism, is a tightly packed mass of hydroxyapatite crystals in an organized pattern (**Heymann et al., 2013**).

Enamel/dentin adhesion is a very critical step of the restorative procedure. Operators should always keep in mind that the use of any form of peroxide (bleaching agents but also whitening mouthrinses, toothpastes, strips, etc) will affect the performance of the bond. Patient questionnaires should cover this topic, and patients should be advised to interrupt the use of such products for at least 2 weeks before restorative procedures (**magne and belser, 2022**).

Successful execution of enamel bonding provides the major retentive feature of the restoration even in the absence of another type of mechanical retention or stabilization. The effectiveness of this procedure requires the use of 30% to 37% phosphoric acid for 20 to 30 seconds (fig. 1-7), followed by thorough rinsing and drying before the application of a low-viscosity adhesive resin (to form resin tags) and subsequent polymerization. Enamel is not isotropic, and hence the walls of the preparation should be contoured to give transverse sections of enamel prisms, which will provide significantly higher bond strength than longitudinal sections of enamel prisms, The topography of the resin tags therefore vary with the location on a tooth and are dependent on the orientation of prepared cavity (**magne and belser, 2022**).



(fig. 1-7) (**magne and belser, 2022**).

1.9 Dentin Adhesion

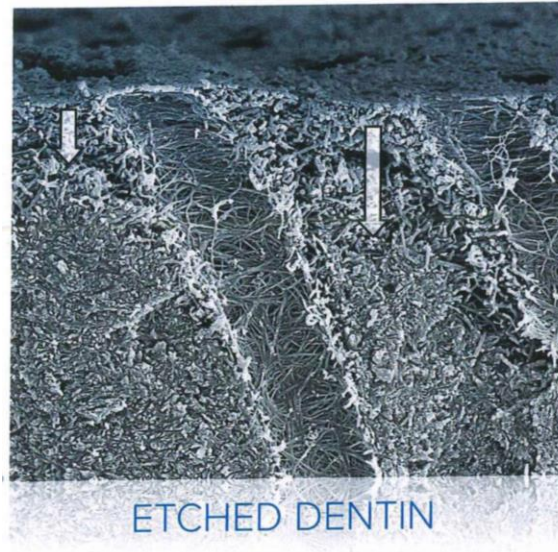
Because the structure of dentin is complex, there are many problems regarding bonding with dentin.

1. Dentin are hydrophilic and saturated oxygen.
2. Dentin continues to form throughout life.
3. Mineral phase (70%), organic phase (30%).
4. Its complex structure varies from the depth of the tubule. In fact, near the dentinoenamel junction, only 1% dentinal tube is present on the dental surface and 22% dentinal tube is near the pulp.
5. Dentin is covered by dentin mud, It should be noted that the removal of dentin by milling creates a deposit smear layer.

Therefore, these obstacles make it difficult to develop reliable dental adhesive systems (Sofan et al., 2017).

Hence, it seems advisable to mimic the roughness of the DEJ when preparing the dentin for bonding. Carbide burs can only produce smooth surfaces. Instead, systematic use of coarse diamonds for dentin preparation is recommended prior to dentin bonding, and even more so when bonding to biocorroded ("eroded") dentin,"s (magne and belser, 2022).

Following preparation, the dentin is covered with a smear layer (debris of collagen and minerals), which impedes the bonding process. The two approaches available to remove the smear layer define the main families of modern dentin bonding systems: the total-etch approach and the self-etch approach (fig.1- 8) (magne and belser, 2022).



(fig. 1- 8) SEM of excavated dentin (cross-sectional view). The depth of demineralization from intertubule dentin is approximately $2-5 \mu\text{m}$ (arrows). (Photo courtesy of Professor Jorge Berdjao, University of Minnesota.) (**magne and belser, 2022**)

1.1 • Conditioning of Dentin

It is defined as an alteration of the dentin surface including the smear layer with the objective of producing a substrate capable of micromechanical and possibly chemical bonding to a dentin adhesive. The principal effects of conditioning on dentin can be physical or chemical. Conditioning can be performed by chemical, thermal or mechanical means (**Sikri V K, 2017**).

1. Chemical Conditioning: Both acids (e.g., 37% phosphoric acid is routinely used) and calcium chelators, which rely on removing the smear layer are used as chemical conditioners.
2. Thermal Conditioning: Lasers are being used to condition dentin the commonly used Lasers are CO₂ and Nd: YAG Laser.
3. Mechanical Conditioning: Micro-abrasion is used to mechanically condition the dentin. (**Sikri V K, 2017**).

1.11 Challenges in Dentin Bonding

Substrate bonding to enamel is a relatively simple process, without major technical requirements or difficulties. Bonding to dentin presents a much greater challenge. Several factors account for this difference between enamel and dentin bonding. Enamel is a highly mineralized tissue composed of more than 90% hydroxyapatite, whereas dentin contains a substantial proportion of water and organic material, primarily type collagen. Dentin also contains a dense network of tubules that connect the pulp with the dentin enamel junction (DEJ) (**Manuja et al., 2012**). A cuff of hypermineralized dentin called peritubular dentin lines the tubules. The less mineralized intertubular dentin contains collagen fibrils with the characteristic collagen banding. Dentin is an intrinsically hydrated tissue, penetrated by a maze of fluid-filled tubules. Movement of fluid from the pulp to the DEJ is a result of a slight but constant pulpal pressure. Pulpal pressure has a magnitude of 20-30 mm Hg (**Terkla et al., 1987**). Dentinal tubules enclose cellular extensions from the odontoblasts and are in direct communication with the pulp. Adhesion can be affected by the remaining dentin thickness after tooth preparation. Bond strengths are generally less in deep dentin than in superficial dentin (**Sattabanasuk et al., 2004**). Whenever 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 by nearly 90%. Removal of the smear layer and smear plugs with acidic solutions results in an increase the fluid flow onto the exposed dentin surface. This fluid can interfere with adhesion because hydrophobic resins do not adhere to hydrophilic substrates, even if resin tags are formed in the dentin tubules. All of these variables make dentin dynamic substrate and consequently a difficult substrate for bonding (**Heymann et al., 2013**).

1.12 Role of Smear Layer in Dentin Bonding

Smear layer is a zone of tooth preparation debris found spread on the surface after tooth preparation. Some of this debris blocks the orifices of the dentinal tubules, forming smear plugs that decrease the dentin permeability by 86%. However, the fluid from the dentinal tubules can permeate through the smear layer due to its micro-porous structure. The smear layer is mainly composed of

hydroxyapatite and collagen that is denatured by the friction and heat during tooth preparation, It has been suggested that the smear layer should be removed prior to the application of the bonding agent. Complete removal and partial removal of the smear layer are observed when phosphoric acid is used in etch-and-rinse adhesives and self-etching adhesives, respectively (**Saikaew et al., 2022**).

Prior to the use of phosphoric acid, dental adhesives in the early generations bonded directly to the smear-covered surface . The in vitro bond strengths of these adhesives have been reported to be less than 10 MPa, which could easily result in clinical debonding (Eick et al., 1991). The debonded specimens were also mainly classified as cohesive failure within the smear layer because the adhesive resin was hydrophobic and, therefore, failed to penetrate through such a zone of debris (**Saikaew et al., 2022**).

1.13 Configuration or "C-factor"

The cavity configuration, or C-factor, was introduced by Prof. Carol Davidson and his colleagues in 1980s. The configuration factor (C-factor) is the ratio of bonded surface of the restoration to the unbonded surfaces (**Feilzer et al., 1987**).

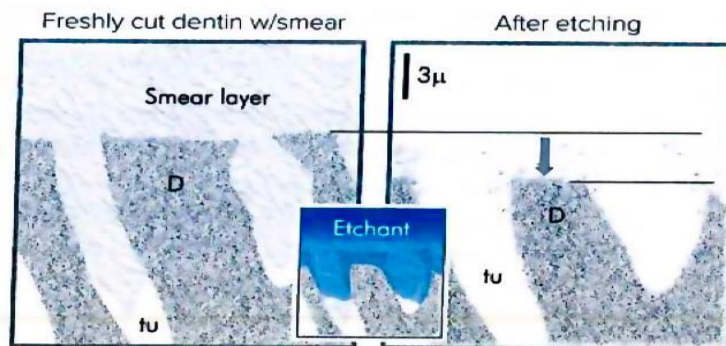
The C-factor can be used to predict which restorations are most likely to exhibit bond failures between the resin and the tooth. According to Feilzer et al., restorations with a C-factor less than one are more likely to survive polymerization contraction stresses and remain bonded to the tooth. This may be a problem, because Class preparations have a mean C-factor of 1.0 and Class II preparations have a mean C-factor of 1.8 (De la Marcorra and Gomes Fernandez, 1996). The negative effect of C-factor is supported by He et al. (2007), who reported that bulk filling a cavity with a C-factor of five produced the lowest bond strength: more microleakage has been reported as the C-factor increases. An in vivo study has also reported that the resin-dentin interdiffusion zone was detached from the overlying resin in restorations with a C-factor of five. Consequently, the higher the value of C-factor, the greater is the polymerization shrinkage. Therefore, three-dimensional tooth preparations (Class I) have the highest (most unfavorable) C-factor and thus are at more risk to the effects of polymerization shrinkage (**Perdigao et al., 1996**).

1.14 Bonding Agent Constituents

1.14.1 Etchants

In total-etch technique the etchant used is 30-37.5 % phosphoric acid. It prepares enamel and dentin to receive the primer. It creates micro-porosities, Smear layer removed, 2-8 microns of dentin demineralized when leaves it 10-15 sec then Abundant rinsing and gentle air-drying (Fig. 1-9) (Magne and Belser, 2022).

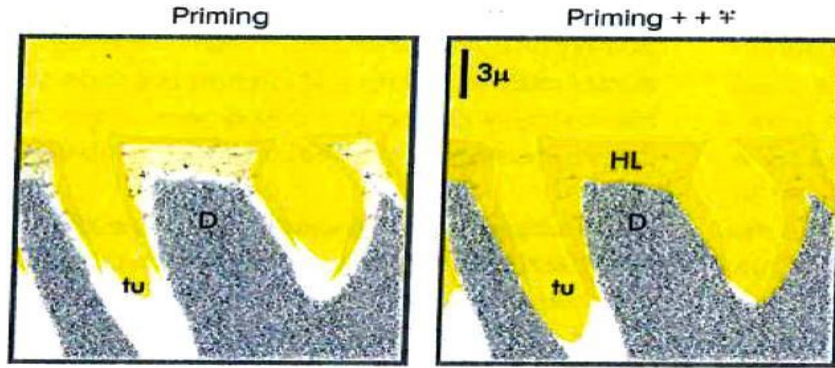
The etchant in self-etch bonding agents is typically an acidic monomer that also serves as the primer (Sofan et al., 2017).



(Fig. 1-9) (Magne and Belser, 2022)

1.14.2 Primers

Priming is the second step in bonding procedure. The primer is composed of hydrophilic monomers usually carried in a water-soluble solvent (acetone, ethanol, water) to promote good flow and penetration into hydrophilic dentin, which can influence the resulting bond strength. Self-etch bonding agents utilize primers that are acidic monomers (Fig. 1-10) (O. Kiuru et al., 2021).



(Fig. 1-10) (Functional, hydrophilic monomers with water/alcohol solvents) Scrubbing motion for 10 sec (repeat 2-3x), gentle air-drying (surface should look shiny but without liquid film).
 → Infusion of hydrophilic and functional monomers → Hybrid layer (**magne and belser, 2022**).

1.1.4.2.1 Methacrylic acid (MA)

Methacrylic acid is rarely used because of its irritant and corrosive properties and this is attributed to its high acidic property that can infiltrate gloves and cause allergic effect on the skin (**Hayakawa et al., 1998**).

1.1.4.2.2 Hydroxyethyl methacrylate (HEMA)

HEMA (2-hydroxymethyl methacrylate) exhibit hydrophilic properties. Also, because most of the acidic monomers are low water-soluble and to increase the wettability of dentin surface, seeks to improve infiltration of the exposed collagen network, which is inherently humid. It also assists in the penetration of liquid filled dentinal tubuli. They bonded to dentin by surface wetting and interaction between their phosphate groups and calcium ions in the smear layer. This has been reported to result in an immediate improvement of bond strength (**kugel and macro, 2000; Pashley, 2003**) However, HEMA is affected by moisture greatly and this makes it easily contaminated with water and cause the absorption of water in the cured and the uncured state. The contamination with water before curing will cause the dilution of the monomer and this will lead to the inhibition of polymerization. The absorption of water after curing will cause discoloration and swelling. Moreover, the increased concentration of HEMA in

them adhesive will cause decrease the quality and mechanical properties of the resulting monomer (**Patel et al., 2000**).

1.1.4.2.3 [10-methacryloyloxy-decyl-dihydrogen-phosphate (10-MDP)]

1) It is acidic nature (they are esters of phosphoric acid) gives them the potential to etch and demineralize tooth tissues, which makes them good candidates for use in adhesives that require self-, selective-, and total-etching options (**Alex and Gary, 2010**).

2) It is bond chemically to metals, zirconia, and to tooth tissues through the formation of non-soluble Ca^{+2} salts (**Moura and Sandra, 2006**). It is a versatile functional monomer with a hydrophobic methacrylate group on one end (capable chemical bonding to methacrylate-based restoratives and cements) and a hydrophilic polar phosphate group on the other. This attribute alone makes it desirable for use in a "universal" adhesive (**Alex and Gary, 2010**).

3) It is the most hydrophobic of all the functional monomers typically used in dental adhesives (**Suh and Byoung, 2013**). This may be important in terms of the adhesive durability, as water sorption and hydrolytic breakdown interface over time has been implicated as one of the primary causes of bond failure. The hydrophobic nature of 10-MDP also makes it relatively stable in solution, which is important in terms of shelf-life (**Hashimoto et al., 2004**).

4) Additionally, 10-MDP is one of the few monomers used in adhesive dentistry that has been shown to actually bond chemically to the tooth tissues via ionic bonding to calcium found in hydroxyapatite (**Fukegava et al., 2006**). Stable MDP-calcium salts are formed during this reaction and deposited in self-assembled Nano-layers of varying degrees and quality depending on the adhesive system (**Yoshihara et al., 2014**).

1.1.4.3 Solvent

Solvents are substances capable to dissolve or disperse one or more substances. They govern the viscosity to some extent. They also control the diffusion capability of the bonding agent. Ethanol, acetone and water are the most commonly used solvents. These solvents should completely vaporize and should not remain as it will affect polymerization as it will dilute monomers and may

result in porosities and increase the permeability of the adhesive layer. The vapour pressure of the solvent controls the evaporation of the solvent. Multiple times application of primer contributes for a improved adhesion, particularly in dentin. As the solvent evaporates for every adhesive application, the co-monomer concentration increases there by improving the quality of the hybrid layer and the correlation of adhesive layer cured versus no cured due to the oxygen inhibition. Multiple adhesive layers does not contribute to increase the thickness of adhesive layer, but improve the concentration of monomers in the adhesive layer and there by the quality (**Adriana et al., 2017; Betancourt et al., 2019**).

1.14.3.1 Water

The role of water is to provide the medium for ionization and action of these acidic resin monomers. Water is a poor solvent for organic compounds (such as monomers). It can be overcome by addition of a secondary solvent, such as ethanol and acetone (**katta, 2020**). Water is a strong polar solvent that will form a hydrogen bond and have a high dielectric constant that gives it the ability to dissolve ionic lattices and polar compounds. On the other hand, it is a poor organic solvent such for monomers which is usually hydrophobic compounds. Due to this problem, mixing of another solvent such as ethanol or acetone has solved this problem. Water is very important solvent because it is the only solvent that is capable of re-expanding the collagen fibers due to the high dielectric constant and a must found solvent in the self-etch adhesives for the ionizing of the acidic monomer (**Carvalho et al., 2003**). Moreover, it was shown that monomers, such as HEMA, decrease the vapor pressure of water even more, which may interfere with the removal of the last amounts of water. It was shown that excess water in the adhesive resin compromises the bond strength of adhesives due to entrapment of water blisters ('over wet phenomenon') (**Pashley et al., 1998**).

1.14.3.2 Ethanol

Ethanol falls in the same category of water as a polar solvent. However, it has lower dielectric and has a higher vapor pressure compared to water which facilitate its evaporation with air drying. When ethanol and water are mixed as two solvents in the same adhesive they create a mixture that is called azeotropic.

The explanation of this phenomenon is that a hydrogen bond is created between water and ethanol that makes it easier for these solvents to evaporate than water alone (**Moszner et al., 2005**). Moreover, it was found that ethanol can keep a greater space between the collagen fibers after the evaporation and this could be due to its stiffening effect on the demineralized collagen (**Fukegawa et al., 2006**).

1.14.3.3 Acetone

Acetone is an apolar solvent that combines a high dipole moment and a low dielectric constant, which gives it the ability to dissolve polar and apolar substances and due to this acetone is considered to be solvent for adhesives that contain hydrophobic and hydrophilic compounds. One advantage of acetone is the evaporation time due to its relatively high evaporation pressure which is considered to be four times greater than ethanol. However, this could affect the shelf life of adhesive containing acetone. Azeotrope is also formed when acetone is used in combination with water. Moreover, acetone has a water chasing feature that increases the removal of water (**Jacobsen and Söderholm, 1995**).

1.14.4 Adhesives

For dentin bonding, the primary purpose of adhesives is to fill the interfibrillar space of the collagen network, creating a hybrid layer and resin tags to provide micromechanical retention upon polymerization. In addition, adhesive layers also should prevent fluid leakage along the restorative material's margin, since they make up the major part of the intermediate layer between dentin and/or enamel and restorative composites (**Anusavice et al., 2013**). It is evident that adhesives need to be hydrophobic so that fluid will not be allowed to permeate through the intermediate layer. At the same time, adhesives require a certain hydrophilicity to diffuse into the hydrophilic, primer-wetted dentin. Generally, adhesive resins are composed mainly of hydrophobic dimethacrylates such as Bis-GMA, TEGDMA, and urethane dimethacrylates (UDMA), and a small amount of a hydrophilic monomer such as HEMA (**Anusavice et al., 2013**).

1.14.5 Initiators

Similar initiator systems are used in both adhesives and restorative composites. Polymerization can be initiated either through a photo initiator system consisting of a photosensitizer (e.g., Camphorquinone) and an initiator (e.g., tertiary amine), through a self-cure system that includes a chemical initiator (e.g., benzoyl peroxide), or through a dual-cure initiator system (**Anusavice et al., 2013**). Most important characteristics of photo-initiators are their peak absorption wave length and their absorption spectrum. Photo-initiators absorbing in the visible light spectrum are usually used. Also, the maximum absorption wavelength varies based on the solvent, in which the photo-initiator is dissolved (**katta, 2020**).

1.14.6 Inhibitors

They are added to prevent the initiators from auto reaction specially in hard storage condition as during shipping and transporting and as a result increase the shelf life of adhesive (**Odian G, 2004**).

1.14.7 Fillers

Recently nano-fillers have been added ranging from 0.5% to 40% by weight in the 4th generation adhesive systems. Fillers control handling and may improve strength. Fillers may increase film thickness of the adhesive layer. In the new agents, the addition of nano-fillers with an average particle size of 12 nm increases the penetration of resin monomers and the hybrid layer thickness, which in turn improves the mechanical properties of the bonding systems. The type of nano-fillers and the method that these particles are incorporated affect the adhesive viscosity and penetration ability of the resin monomers into collagen fibers spaces. Nano-fillers, with dimensions larger than 10-20 nm or a content of more than 10 percent by weight, both can increase the viscosity of the adhesives, and may cause accumulation of the fillers over the top of the moistured surface. These clusters can act as flaws which may induce cracks and cause a decrease in the bond strength (**Sofan et al., 2017**).

1.14.8 Other Ingredients

A number of additional ingredients are used with dentin bonding agents for a variety of specific purposes. A few examples include the following:

glutaraldehyde is added as a desensitizer. Fluoride is added to prevent secondary caries. Chlorhexidine are used to prevent collagen degradation (**Anusavice et al., 2013**).

1.10 Classification

Over the years, there have been numerous classifications of dentin bonding agents that have been advocated by many authorities. Some of them are based on generation, the number of clinical steps and on the modern adhesive strategy (**Sofan et al., 2017**).

1.10.1 Classification by generation

1.10.1.1 First Generation

The first generation bonding systems were published by Buonocore in 1956, who demonstrated that use of glycerophosphoric acid dimethacrylate (NPG-GMA) containing resin would bond to acid etched dentin. These bonding agents were designed for ionic bonding to hydroxyapatite or for covalent bonding (hydrogen bonding) to collagen. Overall, this generation leads to very poor clinical results as well as low bond strength in the 1-3 MPa range (**Sofan et al., 2017**).

1.10.1.2 Second Generation

The second generation dentin bonding agents were developed in the late 1970's and early 1980's (**Kugel et al., 2000**). These systems leave the smear layer largely, if not wholly, intact when used. Second generation bonding agents produced variable results; they generally performed better than first-generation bonding agents (**Bart et al., 2006**). This generation of bonding agents is no longer used, due mainly to failed attempts to bond with a loosely bond smear layer. Bond strength: 4-6 Mpa (**Sofan et al., 2017**).

Drawbacks in the First and Second Generation: The reasons for limited success of these generations of bonding agents include: (**Sikri V K, 2017**).

1. Lack of adequate bond strength that could overcome contraction stresses during polymerization.
2. Being hydrophobic in nature, close adaptation to the hydrophilic dentin could not be achieved.

- ϣ. Biocompatibility was not appropriate.
- ξ. Lack of sufficient knowledge about the presence and nature of smear layer
Moreover, the adhesive bonded to the smear layer rather than the dentin
As result the bond achieved was limited by cohesive failure in the smear layer or a break at the smear layer-dentin interface.

1.15.1.3 Third Generation

In the late 1970s and early 1980s, third generation dentin bonding agents were presented. The third generation bonding systems introduced a very important change: the acid etching of the dentin in an effort to modify or partially remove the smear layer. This opened the dentin tubules and allowed a primer to be placed after the acid was completely rinsed away. Bond strength: 12-10 Mpa (Sofan et al, 2017).

Drawbacks in the Third Generation Bonding Agents Clinical studies showed decrease in retention with time. So the main problem was the longevity of the maintenance of the bond. These are technique sensitive and time consuming (Sikri V K, 2017).

1.15.1.4 Fourth Generation (Three-step etch-and-rinse adhesives)

In 1980s and 1990s, fourth generation dentin bonding agents were introduced. The fourth generation materials was the first to achieved complete removal of smear layer and still considered as the golden standard in dentin bonding. In this generation, the three primary components (etchant, primer and bonding) are typically packaged in separate containers and applied sequentially. The concept of total-etch technique and moist dentinal hallmarks of the 4th generation systems, where dentin and enamel are etched at the same time with phosphoric acid (H_3PO_4) for a period of 10-20 s (Kugel et al., 2000).

Advantages of this concept of bonding agents are:

- 1. Reduced technique sensitivity.
- 1. Similar bond strengths to enamel and dentin.

۲. No reduction in bond strength when applied to moist surface or under conditions of high humidity and some systems can bond to mineralized tissue as well as metal, amalgam, porcelain and indirect composite restorations (**Sikri V K, ۲۰۱۷**).

۱.۱۵.۱.۵ Fifth Generation (Two-step etch-and-rinse adhesives)

Because of the complexity and number of steps of compounds involved with the fourth-generation systems, researchers and manufacturers have worked to develop simpler adhesive systems (**Tay et al., ۱۹۹۶**). In the ۱۹۹۰s and in the ongoing decade, the fifth generation bonding systems sought to simplify the process of fourth generation adhesion by reducing the clinical steps which results in reduced working time. They involve the application of phosphoric acid followed by rinsing with water, followed by priming and bonding the dentin and enamel simultaneously where the resin and the primer components are mixed in one bottle, followed by air-drying and polymerization (**De Munck et al., ۲۰۰۵**). These kinds of adhesives systems may be more susceptible to water degradation over time than the fourth generation. This is because the polymerized primer of the "one bottle system" tends to be hydrophilic in nature. However, when using the fourth generation, the hydrophilic primer is covered by a more hydrophobic resin, making it less susceptible to water sorption. Bond strength: ۲۰Mpa (**Sofan et al., ۲۰۱۷**).

۱.۱۵.۱.۶ Sixth Generation (Two step self-etch adhesives)

The sixth generation bonding systems introduced in the latter part of the ۱۹۹۰s and the early ۲۰۰۰s also known as the "self-etching primers", were a dramatic leap forward in technology. The sixth generation bonding systems sought to eliminate the etching step, or to include it chemically in one of the other steps: (self-etching primer + adhesive) acidic primer applied to tooth first, followed by adhesive or (self-etching adhesive) two bottles or unit dose containing acidic primer and adhesive; a drop of each liquid is mixed and applied to the tooth (**Pashley et al., ۲۰۰۲**). The biggest advantage of the sixth generation is that their efficacy appears to be less dependent on the hydration state of the dentin than the total-etch systems. Bond strength: ۲۰Mpa (**Sofan et al., ۲۰۱۷**).

1.15.1.7 Seventh Generation (One-step self-etch adhesives):

The seventh generation bonding systems was introduced in late 1999 and early 2000. The seventh generation or one-bottle self-etching system represents the latest simplification of adhesive systems. With these systems, all the ingredients required for bonding are placed in and delivered from a single bottle (Alex and Gary, 2008). In this type of adhesive, the hydrophobic adhesive monomer and acidic primer came in one bottle, which primes conditions and infiltrates the enamel and dentine before polymerization. Bond strength: 20-30 Mpa (Sofan et al., 2017).

1.15.1.8 Eighth Generation

In 2010, voco America introduced voco futurabond DC as 8th generation bonding agent, which contains nano-sized fillers. In the new agents, the addition of nano-fillers with an average particle size of 12 nm increases the penetration of resin monomers and the hybrid layer thickness, which in turn improves the mechanical properties of the bonding systems (Başaran et al., 2009). Nano bonding agents are solutions of nano-fillers, which produce better enamel and dentin bond strength, stress absorption, and longer shelf life (Nair et al., 2014). The type of nano-fillers and the method that these particles are incorporated, affect the adhesive viscosity and penetration ability of the resin monomers into collagen fibers space.

Nano-fillers, with dimensions larger than 10-20 nm or a content of more than 10 percent by weight, both can increase the viscosity of the adhesives, and may cause accumulation of the fillers over the top of the moistured surface. These clusters can act as flaws which may induce cracks and cause a decrease in the bond strength. Bond strength :> 30 Mpa (Kasraei et al., 2009).

Table 1-1 chronologic adhesive milestone and generation of dentin bonding systems (Magne and Belser, 2022).

1951	First adhesive monomer. glycerophosphate dimethacrylate (GPDM) by Hegger (Switzerland)
1952	First-generation adhesive With GPDM (Sevriton, Kramer, and McLean. I-JK) (1952)
1955	Enamel etching (Buonocore, USA)
1956	Dentin etching with 10% phosphoric acid for 30 seconds (Buonocore) (1956)
1960s	Concentration reduced to 30% for 20-30 seconds
1970s-1980s	Second-generation, smear layer maintained but poor results (0.6 MPa)
1979	Removing the smear layer (Fusayama et al. Japan) (1979)
1980s	Third-generation. modified or completely removed smear layer
1982	Hybrid layer (Nakabayashi et al.)
Late 1980s	Fourth-generation. three step (etch-and-rinse)
Early 1990s	Fifth-generation. two-step (etch-and-rinse)
Late 1990s	Sixth-generation, two-step (self-etch) and me-step (with mixing)
2000s	Seventh-generation, one-step (Without mixing)
2010s	Eighth-generation, multimode universal adhesives (etch-and-rinse or self-etch) With IO.MIP (10-MDP, 10-methacryloyloxydecyl dihydrogen phosphate).

1.1.2 Classification by mechanism of adhesion/clinical step

At this stage it was proposed a classification of bonding systems (fig. 1-11), which reflects their essential mode of use, rather than historical development:

1.1.2.1 Total-Etch adhesive strategy (Etch and Rinse)

It includes two types of adhesives according to the number of steps involved:

A-Three-steps: involving etch, prime and bond. These bonding systems are supplied as three bottles, one each from etchant, primer and bonding agent. These are the most complicated to use in the clinic, but result in highest bond strengths and greatest durability (Eshrak et al., 2017).

B-Two-steps 1: here the steps are etch, then finally prime and bond in a single coating. Bonding systems of this type employ substances in two bottles, one consisting of etchant, and the other of the combined prime and bond formulation (Eshrak et al., 2017). The solvent present in such adhesives is also more difficult to evaporate, frequently remaining entrapped within the adhesive layer after polymerization (Van Meerbeek et al., 2005).

1.1.2.2 Self-Etch adhesive strategy (Non-Etch and Rinse)

The etching pattern on unground enamel depends on the aggressiveness of the self-etch adhesive used, ranging from absent to moderate (Perdigao et al.,

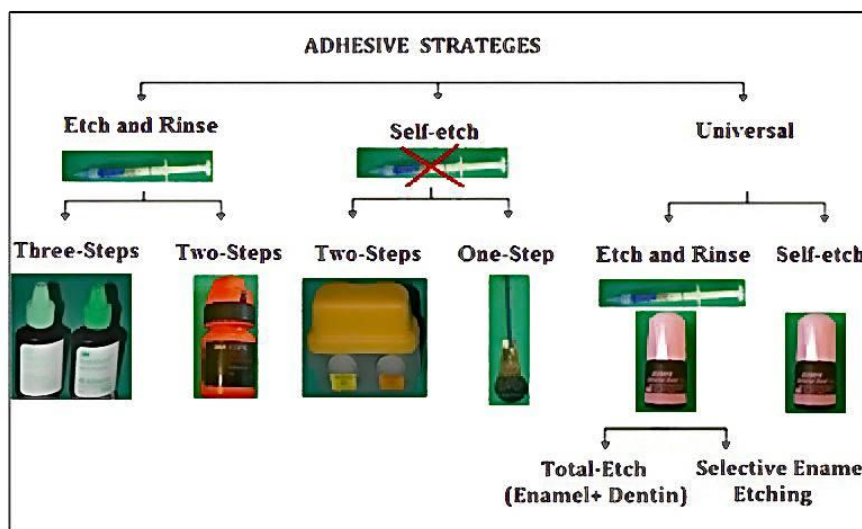
۲۰۰۳). Self-etch adhesives are unable to etch enamel to the same depth as phosphoric acid due to their lower pH (**Perdigão et al., ۲۰۰۵**). Self-etching systems were introduced to control the sensitivity to humidity of the etch-and-rinse technique as well as to simplify the clinical procedures of adhesive application, reducing clinical time (**Sundfeld et al., ۲۰۰۵**).

A-Two-steps ۲: for these systems, the two steps are etching and priming combined followed by bonding. It uses two bottles of components, the first containing a self-etching primer and the second the bonding agent. The self-etching primer modifies the smear layer on the surface of the dentine, and incorporates the products in the coating layer (**Eshrak et al., ۲۰۱۷**).

B- One-step: this uses a single bottle containing a formulation that blends a self-etching primer and bonding agent. Clinically, this is the easiest to use, and bond strengths are generally reported to be acceptable, despite the simplicity of bonding operation (**Eshrak et al., ۲۰۱۷**).

۱.۱۵.۲.۳ Universal adhesive systems

One of the most recent novelties, in adhesive dentistry, was the introduction of universal adhesives that have been used since ۲۰۱۱ in clinical practice. These new products are known as "multi-mode" or "multi-purpose" adhesives because they may be used as self-etch (SE) adhesives, etch-and-rinse (ER) adhesives, or as SE adhesives on dentin and ER adhesives on enamel (a technique commonly referred to as "selective enamel etching") (**Hanabusa et al., ۲۰۱۲**).



(fig. ۱-۱۱) (**Eshrak et al., ۲۰۱۷**).

1.16 Luting Agents And Resin Cements

For many years, retention of indirect restorations could only be attained by the use of favorable tooth preparations and by micromechanical interlocking of the luting agent into irregularities present on the surface of the restoration and the tooth. Adhesive bonding completely changed the use of direct and indirect restorations. A number of materials are available for cementation, including zinc phosphate cements, polycarboxylate cements, glass-ionomer cements (GIC), RMGI cements, and resin cements (**Anusavice et al ., 2013**). The choice of luting agent is dependent on clinical factors including dental occlusion, tooth preparation, adequate moisture control, core material, supporting tooth structure, tooth location (**Özcan, 2013**). Resin cements must bond to different substrates, including tooth structure, resin composites, gold, metal alloys, titanium, and porcelain, and other ceramics. Resin cements can follow the application dentin bonding agents or not when bonding to tooth structure. The former can be considered either as etch-and rinse adhesive resin cement or as self-etch adhesive resin cement, according to its bonding agent system (**Anusavice et al., 2013**).

1.17 Amalgam Bonding

Bonding of amalgam restorations has proved to enhance the strength and reduce the microleakage of the bonded amalgam restorations compared to the nonbonded or conventional amalgam restorations. The bonding agent's viscosity also plays an important role in the increased retention by means of an interlocking mechanism. The amalgam mix produces interlocking projections into the bonding agents for improved mechanical retention and also amalgam bonding agents have clinically proven that they are capable of reducing microleakage associated with conventional restorations (**Anuj, 2011**).

1.18 Pit and Fissure Sealants

Dental sealants were introduced in the 1960s to help prevent dental caries in the pits and fissures of mainly the occlusal tooth surfaces. Sealants act to prevent the growth of bacteria that can lead to dental decay (**Ahovuo-Saloranta et al., 2013**). Various materials and techniques have been advocated for preventing caries in the susceptible pit and fissure areas of posterior teeth, particularly in the

pediatric patient or for the patient at a high caries risk in general. The most popular sealant techniques make use of resin systems that can be applied to the occlusal surfaces of teeth (**Anusavice et al., 2013**).

1.19 Orthodontic Bracket Bonding Resins

Orthodontic treatment with fixed appliances involves the use of attachments such as brackets and bands. Bands are metal rings that go around teeth and are usually used on molars. Brackets can be welded to bands but are most commonly used today bonded to enamel. The development of bonding has contributed to a decrease in banding even in posterior teeth. A variety of luting agents have been used in orthodontics such as polycarboxylate cement, GIC, and resin modified glass ionomer (RMGI) cements (**Anusavice et al., 2013**). Considerable interest has been shown in the method of bonding orthodontic attachments directly to the tooth surface eliminating the use of bands. Many orthodontists are using this technique routinely in clinical practice (**Reynolds, 1975**).

1.20 Conclusion

Advances in adhesive dental technology have radically changed restorative dentistry. Bonding between tooth and the restorative material should be good. Various techniques have been mentioned to achieve this goal. Following the correct clinical procedure and using the right material contributes to the success of bonding. The advent of new resin technologies like self-etching primers, simplified the procedure and is comparatively less technique sensitive than the total etches technique. However long term clinical studies are essential for the material.

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