ADHESIVE SYSTEMS: A CRITICAL LOOK AT THE SCIENCE BEHIND ADHESION

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Álefi Marques Lopes da Silva[1], Carolina Cardoso de Araujo[2], Sarah de Araújo Mendes Cardoso[3], Geovanna de Castro Bizarria[4], José Lucas dos Santos Silva[5], Marcelo Lopes Silva[6], Maria do Amparo Veloso Magalhães[7], Maria Sarah Teresa Lima Verde Moura[8], Marine Olmos Villagomez[9], Ousanas Wesllen Macedo da Costa[10], Nicollas Gabriel de Carvalho Lima[11] and Wglanna Kellen de Maria Silva Costa[12].

ABSTRACT

Adhesive systems play a crucial role in restorative dentistry, providing significant advancements from their introduction to modern technologies. Historically, its evolution reflects the search for greater adhesive efficiency and simplification of clinical protocols. The dental structure, composed of enamel and dentin, has distinct characteristics that influence adhesion. Enamel is highly mineralized, with high-energy surfaces, while dentin is less mineralized, has higher organic content, and dentin fluid, presenting additional adhesion challenges. Adhesive systems chemically interact with these substrates, using monomers, solvents, and primers that promote wettability and copolymerization. Its physical properties, such as viscosity and penetrability, and mechanical properties, such as shear strength, ensure the durability of restorations. The classification of adhesive systems, either by number of steps or by the form of interaction with the substrate, offers criteria for the selection of the most appropriate material. Constant innovation in these systems aims to optimize clinical outcomes, promoting aesthetic, functional, and durable restorations. The integration of scientific knowledge and clinical practice is essential for the continued development of more effective adhesives.

Keywords: Dentin Adhesives. Tooth Enamel. Hydroxyapatite. Dental Photoinitiators. Dentin.

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[1] Master's student, Ribeirão Preto School of Dentistry, University of São Paulo (FORP/USP)
alefi1968@gmail.com
[2] Master's student, Ribeirão Preto School of Dentistry, University of São Paulo (FORP/USP)
carolinacodonto@outlook.com
[3] Master's student, Piracicaba Dental School, State University of Campinas (UNICAMP)
s290973@dac.unicamp.br
[4] Master's student, Piracicaba Dental School, State University of Campinas (UNICAMP)
geovannabizarria@gmail.com
[5] Dental Surgeon, Faculty of Dentistry CECAPE
joselucassilva52tg@gmail.com
[6] Master's degree, Federal University of Maranhão, UFMA
marcelopesilva@hotmail.com
[7] Dr., Lutheran University of Brazil
amparovm@bol.com.br
[8] Master's student, Federal University of Piauí
masarah144@gmail.com
[9] Master's student, Ribeirão Preto School of Dentistry, University of São Paulo (FORP/USP)
marine.olmos@usp.br
[10] Undergraduate, Centro Universitário Santo Agostinho
ousanaswesllen@gmail.com
[11] Undergraduate, Centro Universitário Santo Agostinho
nicollasgabriell28@gmail.com
[12] Dental Surgeon, Santo Agostinho University Center
wglanna@hotmail.com

INTRODUCTION

With the advancement of modern restorative dentistry, several adhesive systems have been introduced over the years, however, unresolved questions persist regarding the durability of the resin-dentin bonding interface. Adhesion to enamel structures has been consolidated as a predictable and well-established procedure, while adhesion to dentin, due to its structural and histological complexity, continues to represent a significant challenge. The heterogeneity of dentin, characterized by variability in its composition and structure, can compromise the efficacy of adhesive systems, leading to inconsistent clinical results.

HISTORICAL TWO ADDUCIVE SYSTEMS

The history of dental adhesives dates back to 1949, when Dr. Hagger, a Swiss chemist working at DeTrey/Amalgamated Dental Company, applied for a patent for the first dental adhesive. At that time, dentin was the only substrate considered for adhesion, in contrast to enamel. In 1951, Hagger patented a material called "Cavity Seal", intended to be used in combination with the chemically curing resin "Sevriton". This product incorporated an adhesive known as glycerol phosphoric acid dimethacrylate, which was polymerized by means of a sulfinic acid initiator, later named "Sevriton Cavity Seal". The adhesive developed by Hagger used acid monomers, which make it possible to etch and interact at the molecular level with tooth surfaces, forming physical and chemical bonds between the restoration and the tooth. The concept proposed by Hagger was quickly adopted by other researchers, resulting in the evolution of different generations of dental adhesives. This development marked the first time that binding to tooth structure became commercially viable, through the formation of an interface that resembles what is currently referred to as the hybrid layer (Söderholm, 2007; Sofan *et al*., 2017; Rawls, 2023)

In 1954, Buonocore conducted pioneering experiments on adhesion to enamel by means of acid etching, focusing on modifying the enamel surface to promote adhesion with filling materials. In 1955, he detailed the use of 85% phosphoric acid as an agent to alter the surface topography of enamel, creating an ideal surface for bonding. This modification not only facilitated the adhesion of restorative materials, but also increased the retention of acrylic resin in cracks and grooves, laying a solid foundation for the development of adhesive techniques in dentistry (Buonocore, 1955; Sofan *et al*., 2017; Rawls, 2023).

DENTAL STRUCTURE AND ADHESION SUBSTRATES

TOOTH ENAMEL

Tooth enamel is the only mineralized tissue with epithelial origin in the human body, and it is also the most mineralized. It is composed of 97% hydroxyapatite, a mineral with a crystalline structure, 2% water, and 1% organic matter, with a predominance of proteins, such as amelogenins and enamelins, as well as carbohydrates and lipids (Reis, 2021; Katchburian; Arana, 1999).

This fabric has a porous and semipermeable structure, which allows the passage of fluids and small molecules. Its chemical formula is expressed as $Ca10(PO4)_{6(}OH)_2$, which reflects its mineral composition. Among its physical characteristics are a high density and hardness, a high modulus of elasticity, but also a low tensile strength and great brittleness (Reis, 2021; Katchburian; Arana, 1999).

Structurally, enamel is formed by enamel prisms that follow an undulating path. When analyzed in different sections, these prisms resemble shapes such as "keyholes" or "tennis rackets". Each prism is formed by groups of billions of fine crystals with a hexagonal shape. The mineral composition and the amount of organic matter in the prismatic and interprismatic regions are very similar (Reis, 2021; Katchburian; Arana, 1999).

While not all prisms reach the enamel surface, the upper areas have crystals arranged in a denser and more inclined manner relative to the enamel below. This surface layer, called the aprismatic layer, is the result of the final activity of the ameloblasts. Their thickness and extent vary, usually decreasing on wear surfaces over time (Reis, 2021; Katchburian; Arana, 1999; Kidd *et al*., 1984; Bertacci *et al.,* 2007; He *et al*., 2011).

As we age, enamel undergoes a gradual loss of thickness, which can reach up to a third of its original value in people over 65. In addition, the enamel of aged teeth tends to accumulate a richer surface layer in fluorides, increase its mineralization, and have a more reduced interprismatic matrix. This makes aged enamel less susceptible to acids, which can affect the treatments performed on this surface (Reis, 2021; Kidd *et al.,* 1984; Bertacci *et al.,* 2007; He *et al.,* 2011).

DENTIN

Unlike enamel, dentin is a mineralized tissue of connective nature, being responsible for most of the tooth's structure. It is covered by enamel at the crown and cementum at the root, and inside it houses the dental pulp, a loose connective tissue composed of cells, collagen fibrils, amorphous intercellular substance, nerves, blood and lymphatic vessels. Dentin, mineralized, is part of a tissue complex with the pulp, having the same embryonic origin, and can be seen as an extension of the pulp, both from an anatomical and functional point of view (Reis, 2021; Katchburian; Arana, 1999).

Dentin is composed of 70% hydroxyapatite in the form of elongated crystals, 20% organic material (with 85% type I collagen) and 10% water, when analyzed by weight. In terms of volume, dentin is made up of 45% mineral, 33% organic matter, and 22% water (Reis, 2021; Xu; Wang, 2012).

From a structural point of view, dentin is formed by dentin tubules, in addition to peri- or intratubular and intertubular dentin. During the process of dentinogenesis, dentin forms around the extensions of the odontoblasts, which retract towards the pulp. The continuous presence of these extensions in the mineralized region results in the formation of tubules, which are filled with dentin fluid. These tubules run through the entire thickness of the dentin, with a sinuous path, and their diameters vary from 2.5 μm, near the pulp, to 1 μm at the amelodentinal junction (JAD). The density of the tubules also varies, being approximately 45,000/mm² near the pulp and 20,000/mm² in the JAD. In percentage terms, the presence of tubules can vary from 1% of the total area near the JAD to 22% near the pulp. Dentin fluid, kept under pressure, moves in response to stimuli, such as touch, temperature changes, or osmotic changes, which is directly related to dentin sensitivity (Reis, 2021; Pashley, 1991; Giannini *et al*., 2001).

The peritubular dentin forms the wall of the dentin tubules, being hypermineralized and with variable thickness, larger near the pulp and without collagen fibrils. With the continuous deposition of peritubular dentin throughout life, the lumen of the tubules tends to decrease, and can be completely obliterated due to mechanical stimuli or cariogenic processes. Intertubular dentin makes up the majority of dentin, occupying the spaces between peritubular dentin columns. It is formed by collagen fibrils arranged perpendicular to the tubules, with the apatite crystallites depositing along the fibrils, with their axes parallel to them (Reis, 2021; Xu; Wang, 2012; MARSHALL *et al*., 1997).

Although the mineral composition of intertubular and peritubular dentin is similar, the mineral-to-matrix ratio is three times higher in peritubular dentin, indicating more intense mineralization in this area. Regarding organic content, intertubular dentin is composed almost exclusively of collagen, while peritubular dentin contains non-collagen proteins (Reis, 2021; Xu; Wang, 2012; Marshall *et al*., 1997).

With aging, there is a gradual reduction in the diameter of the dentin tubules due to the continuous deposition of mineral inside. This process begins around the third decade of life and can result in complete obliteration of the tubules, causing the dentin to become sclerotic. Thus, as we age, there is an increase in the mineral content of dentin (Porter *et al*., 2005; Arola *et al*., 2017).

ADHESION AND DENTAL SUBSTRATES: FROM CHEMICAL COMPOSITION TO CLINICAL BEHAVIOR

Dental adhesives are solutions of resin monomers that make the interaction of the dental substrate of the resin possible (Perdigão, 2007; Sofan *et al*., 2017; Tekce *et al*., 2023). Adhesive systems are composed of monomers with hydrophilic and hydrophobic groups. The former increase the wettability of the dental hard tissues, while the latter allow interaction and copolymerization with the restorative material. The chemical composition of adhesives also includes polymerization initiators, inhibitors or stabilizers, solvents, and, in some cases, inorganic fillers (Van; Kirsten, 2007; Sofan *et al*., 2017).

The mineralized part of the tooth is a complex structure composed of different hard tissues, which have different ultramorphology and composition. Tooth enamel is formed by a solid and hard crystalline matrix, predominantly composed of hydroxyapatite (HAp), which has strong intermolecular forces and a high-energy surface, in addition to containing water and organic material. In contrast, dentin is a biological compound of PAH that surrounds collagen fibers. Dentin is intrinsically moist and has lower hardness compared to enamel, characterized by reduced intermolecular forces and low-energy surfaces (Susin *et al*., 2007; Sofan *et al*., 2017; Rawls, 2023)

In addition, dentin is distinguished from enamel by having a smear layer, significant organic content, and the presence of fluid in the dentin tubules. The density of the dentin tubules varies with the depth of the dentin; Thus, the concentration of water in the dentin is lower in the superficial portion and higher in the deep portion. In superficial dentin, which contains a lower density of tubules, the permeation of the resin in the intertubular dentin accounts for most of the bonding force. In deep dentin, where the dentin tubules are more numerous, the intratubular permeability of the resins contributes to a greater bond strength, evidencing the importance of the interaction between the restorative materials and the dentin structure (Susin *et al*., 2007; Sofan *et al*., 2017; Rawls, 2023).

MEMBERSHIP

The fundamental mechanism of adhesion to the tooth structure can be described as a replacement process, in which the mineral component of the tooth, hydroxyapatite, is replaced by synthetic resins. This accession process takes place in two main stages:

1) The removal of hydroxyapatite to create micropores on the tooth surface;

2) The infiltration of resin monomers into the micropores, followed by their polymerization. As a result, resin extensions establish a micromechanical interlock with the hard tissue of the tooth.

In addition, chemical interactions can occur between resin monomers and the dental substrate, especially in the presence of acidic or chelating functional groups, which can promote additional chemical bonds, increasing the adhesion strength and durability of the restorative interface (Hardan *et al*., 2023; Rawls, 2023)

COHESION

This concept refers to the intermolecular force of attraction between the molecules that make up the adhesive material. This property is crucial for the structural integrity and strength of the adhesive under conditions of clinical use. In dental adhesive systems, cohesion is crucial to the effectiveness of adhesion, since high cohesion ensures that the adhesive maintains its integrity under mechanical and chemical stresses. During adhesive application, cohesion contributes to the formation of a robust interface between the adhesive and tooth surfaces such as enamel and dentin. This property is critical for the stability of the adhesive bond, as inadequate cohesion can result in adhesion failures, such as delamination or degradation of the material over time (von Fraunhofer, 2012; Rawls, 2023)

In addition, cohesion is closely related to the adhesive's rheological properties, such as viscosity and fluidity, which influence the material's penetration into the micropores of the tooth structure. In short, cohesion is a determining factor that affects the strength, durability, and performance of dental adhesive systems, directly impacting the effectiveness of the bond between the restorative material and the dental structure.

ADHESIVE INTERFACE AND BIOFILME

The microorganisms present in the oral cavity adhere to the surfaces of the teeth, forming dental plaque, which consists of a diverse community organized in the form of a biofilm. Biofilms form and interact differently with the different microenvironments of the oral cavity, and this interaction is influenced by changes in the ecology of dental plaque, in the restorative material, as well as in the chemistry and characteristics of the surface. In addition, oral bacteria can induce the biodegradation of resin-based materials through the activity of esterases, resulting in the release of hydrolyzed monomer byproducts. Particularly in adhesive systems, the esterase activity of cariogenic bacteria can degrade polymerized resins, especially in self-etching systems, which have a more hydrophilic chemical composition (Bourbia *et al*., 2013).

Methacrylate phosphate derivatives present in some adhesives, such as 10-MDP, can release acidic polymers that inhibit bacterial growth due to their extremely low pH. In this way, both the hydrophilicity of the adhesive system and its pH can influence bacterial growth. Another factor corresponds to short photocuring times that can result in a lower degree of conversion of monomers to polymers, leaving more residual monomers unpolymerized in the materials and, consequently, increasing colonization by *Streptococcus mutans*. In addition, colonization by *S. mutans* is lower on polished resin surfaces or on nanofilled composite resins (Ionescu *et al*., 2012; Brambilla *et al*., 2014). On the other hand, composite resin surfaces with deep depressions, large irregularities, or exposure of the resin matrix are more prone to biofilm formation.

While proper handling of materials maximizes their performance, intrinsic (such as chemistry, bonding mechanism, and biology) and extrinsic (such as the oral environment) factors will influence the longevity of adhesive restorations. Contamination by saliva and blood during the restorative procedure decreases the strength of the union and should be avoided. In the event of accidental contamination, there are experimentally tested strategies to minimize the negative effects, including surface reconditioning, rinsing and drying of the contaminated area, as well as the application of additional layers of adhesive (Cobanoglu *et al*., 2013; Szesz *et al*., 2016).

COMPONENTS OF ADHESIVE SYSTEMS

FUNCTIONAL MONOMERS

Dental adhesives contain resin monomers similar to those present in composite restorative materials in order to ensure an effective covalent bond between the adhesive and the coating composite. Monomers are considered the most important components of the adhesive. Resin monomers that have two or more polymerizable groups are essential to form a highly cross-linked network, ensuring the strength and stability of the adhesive layer. Functional monomers typically have a functional group, such as hydroxyl groups, and a single polymerizable group, allowing the formation of linear polymeric chains. An example is hydroxyethyl methacrylate (HEMA), a hydrophilic monomer that promotes resin diffusion in the wet collagen network and is commonly found in modern adhesive systems (Moszner *et al*., 2005; Van *et al*., 2007).

In self-etching adhesive systems, the functional groups present in resin monomers are often acidic and play a key role in corrosion of enamel and dentin surfaces. Examples of acidic functional monomers include 4-methacryloyloxyethyl trimellitate anhydride, 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP), and 2-(methacryloyloxyethyl)phenyl hydrogen phosphate. These functional groups, such as carboxyl or phosphate, not only promote self-conditioning, but can also form ionic bonds with the calcium of hydroxyapatite (Yoshida *et al*., 2004; Van *et al*., 2018).

The monomer MDPB (methacryloxydodecylpyridinium bromide), patented by Kuraray, is a compound of the antibacterial agent dodecylpyridinium bromide and a methacryl group (Imazato *et al*., 1995). In contrast to most functional monomers, this molecule is quite hydrophobic, thus ethanol and acetone are the most suitable solvents for this monomer. 10-MDP is the most popular and highly stable acid monomer, a characteristic attributed to the long carbonyl chain that connects the functional and polymerizable groups in its structure. In addition, the phosphate functional group has the ability to form robust ionic bonds with hydroxyapatite, thanks to the low solubility of the calcium salts formed (Bedran-Russo *et al*., 2017; Fehrenbach *et al*., 2021). This monomer has the ability to form robust ionic bonds with calcium, due to the low solubility of the calcium salt formed in its own solution. In this study, 10-MDP was identified as the most promising monomer for establishing chemical bonding with enamel hydroxyapatite or dentin (Türkün, 2003).

Some monomers have a more hydrophobic nature such as bisphenol A-glycidyl methacrylate, triethylene glycol dimethacrylate (TEGDMA), urethane dimethacrylate and bisphenol-A ethoxylated dimethacrylate. There needs to be a difference in molecular weight between resin monomers, as low molecular weight monomers help dissolve high molecular weight monomers, improving the wettability of the resin mixture (Moszner *et al*., 2005).

SOLVENTS

The incorporation of solvents in adhesives is essential for your adhesives, as the natural moisture of dentin only allows for good wettability when a hydrophilic bond is applied. By adding hydrophilic monomers on one side and a solvent on the other, the flow behavior of the adhesive is significantly improved (Van *et al*., 2007).

Solvents are incorporated into the adhesive mixtures to reduce viscosity and facilitate the infiltration of the resinous adhesive, for example, ethanol, acetone and water are used, both of which have low cost, wide availability and good biocompatibility. In acid etching and rinse systems, ethanol plays a crucial role in infiltrating resin monomers into the wet collagen network, as well as aiding in the evaporation of excess water through the formation of water and ethanol aggregates (Chiba *et al.,* 2016).

The presence of residual solvent in the adhesive layers can compromise the polymerization of the adhesive, decreasing its mechanical properties and accelerating degradation over time. Thus, it is essential to perform a complete and thorough drying of the adhesive with air, exceeding the time recommended by most manufacturers, to ensure the removal of excess solvent before light-curing (Bail *et al.,* 2012). Thus, it is possible to state that the efficient evaporation of the solvent is an essential step prior to light curing.

PHOTOINITIATORS

Adhesive systems need to be photocured before the application of the resin composite, in order to achieve an optimal degree of conversion, ensure good mechanical resistance of the adhesive layer and avoid excessive thinning of this layer due to the application of the composite (Yoshida; Greener, 1994). Primers are usually molecules that have atomic bonds with low dissociation energy that will form radicals that will trigger the polymerization reaction.

The photoinitiator system plays significant roles in achieving the bond strength and forming a stable adhesive interface. The traditionally used photoinitiator system, composed of camphorquinone and amine, has hydrophobic characteristics and, therefore, can undergo phase separation, leading to insufficient polymerization of the most hydrophilic portion of the adhesive systems (Abedin *et al.,* 2015). The amount of primer incorporated into adhesive systems varies according to the type of primer and adhesive system, but is usually quite small, being between 0.1% and 1% by weight.

An essential characteristic of photoinitiators is the peak absorption wavelength and absorption spectrum. Photoinitiators that absorb in the visible light spectrum are generally preferred. The absorption of these photoinitiators must be aligned with the emission profiles of dental cure units (Hazlewood; Davies, 1996). In addition, the maximum absorption wavelength can vary depending on the solvent in which the photoinitiator is dissolved, usually shifting to shorter wavelengths as the polarity of the solvent increases (Sun; Chae, 2000).

Studies on the use of alternative photoinitiator systems have led to the introduction of compounds such as diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide and 2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanter-2-yloxy)-N,N,N-trimethyl-1-propanamine (QTX) chloride (Dressano *et al.,* 2016).

SILANE AND SILANIZATION

A silane coupling agent is highly effective in promoting bonding between silica-based restorative materials. Its indications in dentistry include, but are not limited to, the cementation of indirect ceramic and metal restorations, ceramic laminates, ceramic repairs, glass fiber-reinforced resin composites, as well as resin composites with reinforced loading, such as cements and filling materials (Blatz *et al*., 2003; Lee, 2015; Matinlinna *et al*., 2018).

For prehydrolyzed (pre-activated) silane primers in a single vial, the solution may become cloudy over time after the first opening and consequently can no longer be used. This is due to the excessive formation of siloxane oligomers or polymers, which are chemically inactive. Alternatively, the two-flask silane system was developed to extend shelf life and increase initial reactivity. In this system, one vial contains non-hydrolyzed silane monomer dissolved in ethanol, while the other contains aqueous acetic acid. Both are mixed immediately before use, allowing the silane to be hydrolyzed effectively (Piascik *et al*., 2009; Lung; Matinlinna, 2012; Nihei, 2016).

Understand how silane works:

a. A silane coupling agent, which is a trialcoxissilane, contains two functional groups at the ends of its molecular structure, and which connect a non-polymerized resin matrix and an inorganic substrate (surface);
b. Formula of bifunctional silane: L-(CH 2) k -Si-(OR) 3
   * L is an organofunctional group (e.g., methacrylate, acrylate, isocyanate, epoxy),
   * k is a ligand group (spacer) that separates the organofunctional group,
   * The Si and OR atom is a hydrolyzable alcoxyl group (methoxy, ethoxy).
c. At room temperature, silane is activated by acid (acetic acid) to form silanol (SiOH) before they can bind to the inorganic substrate;

Joining steps of resin substrate with silane coupling agents:

a. Formation of the silane and substrate bond — activated by acid
b. Formation of the resin and silane bond—activated by light curing

Silane is acid-activated to form silanol groups that react with the hydroxyl (OH) groups of the substrate surface by a condensation reaction:

(Si-OH + HO substrate ⇒ Si-O substrate)

The reaction between the organofunctional groups of silane (with a C=C bond) and the functional groups of the resin monomers, also containing C=C bonds, is induced by the reactive free radicals generated during the photoactivation of the initiating components present in the resin matrix. As a result, the resin composite and substrate surface are efficiently connected by the silane coupling agent (Eggmann *et al*., 2023).

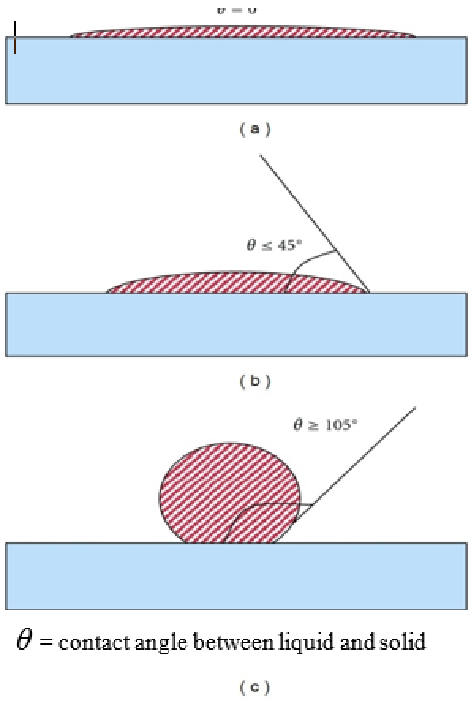
PHYSICAL PROPERTIES OF ADHESIVE SYSTEMS

The physical and mechanical properties of adhesive systems are essential for understanding their performance in dentistry. These properties influence the effectiveness of adhesion, the durability of the restorations, and the resistance to different types of stresses.

WETTABILITY, CONTACT ANGLE, SURFACE TENSION AND SURFACE ENERGY

Materials that wet against each other tend to have a larger contact area than those that do not, however, wettability depends on the relative surface energies of the adhesive materials and substrates. Wetting is the ability of a liquid to form an interface with a solid surface and the degree of wetness is evaluated as the contact angle θ (image 1) formed between the liquid and the surface of the solid substrate. This is determined by both the surface tension of the liquid and the nature and condition of the substrate surface. The lower the contact angle and the lower the surface tension of the liquid, the greater the degree of wetness, that is, the liquid droplet will spread over the surface of the substrate as long as it is clean and uncontaminated (von Fraunhofer, 2012; Rawls, 2023). Take a look at the image below:

Fig. 1 - Ângulos de contato líquido/superfície
para superfícies limpas, levemente
contaminadas e contaminadas



Fonte: von Fraunhofer, 2012.

Observe que uma superfície limpa permite um bom molhamento, ou seja, o ângulo de contato *θ* é próximo de 0° (**figura 1a**)

Já com uma superfície levemente contaminada (**figura 1b**) haverá um ângulo de contato maior (*θ* é maior que 0°, mas menor que 90°, ou seja, 0° < *θ* < 90°)

Já com o ângulo de contato entre o líquido e uma superfície contaminada ou com baixa energia superficial excederá 90° (**figura 1c**)

The condition illustrated in figure 1c is often termed dehumidification, characterized by the formation of liquid droplets on the surface of the substrate. The contact angle (θ) is a function of dispersive adhesion, which refers to the interaction between the molecules of the adhesive and those of the substrate, and of cohesion within the liquid adhesive. When the adhesion to the surface of the substrate is intense and the cohesion within the liquid is weak, a high degree of wetness, commonly classified as lyophilic conditions, is observed. In contrast, a combination of poor adhesion and high cohesion, known as lyophobic conditions, results in high contact angles and poor wetting of the substrate surface, leading to the formation of droplets on the surface, rather than the formation of a continuous film of fluid. This dynamic between adhesion and cohesion is fundamental to understand the wetting behavior of liquids at solid interfaces, with significant implications for the effectiveness of adhesive systems in dentistry and other fields of application (von Fraunhofer, 2012).

VISCOSITY

The optimal viscosity of the dentin adhesive is a critical parameter that directly influences the material's performance in adhesion to dentin. The viscosity of each adhesive system developed is different and plays an important role in wettability and spreading speed on a solid surface (Eick *et al*., 1972; Silikas; Watts, 1999; Rosales-Leal *et al*., 2001; Hisamatsu *et al*., 2002).

Viscosity is the measure of a liquid's resistance to flow, and in the context of dentin adhesives, it is crucial for the adhesive's penetration into the microstructures of dentin. An adequate viscosity allows the adhesive to reach surfaces and integrate well with the substrate. The optimal viscosity for dentin adhesives usually ranges between 200 and 500 cP (centipoise) at room temperature. This strip allows the adhesive to flow easily, penetrate dentin microcracks, and form an effective adhesive interface (Eick *et al*., 1972; Silikas; Watts, 1999; Rosales-Leal *et al*., 2001; Hisamatsu *et al*., 2002; Pazinatto et al., 2006).

Low viscosity: Adhesives with lower viscosity (less than 200 cP) tend to have excellent wetting capacity and penetration into dental microstructures. They are most effective at creating an adhesive interface, but they can be difficult to control during application, resulting in leaks or excess material. **High Viscosity:** Adhesives with high viscosity (above 500 cP) may be easier to handle and control, but have limitations in penetrating dentin microstructures. This can result in inadequate adhesion and lower resistance to disintegration.

MECHANICAL PROPERTIES OF ADHESIVE SYSTEMS

The mechanical properties of adhesive systems play a critical role in determining their effectiveness and durability in dental applications. These properties are determinant in the resistance of the interface between restorative materials and dental substrates, directly influencing the longevity of restorations. The ability of adhesives to resist different types of mechanical stress, such as shear, tensile and compression, is essential to ensure the structural integrity of adhesive bonds under functional conditions. Thus, a detailed understanding of the mechanical properties of adhesive systems is critical for the optimization of materials and techniques that aim to improve clinical outcomes and prolong the durability of dental restorations (Bourgi *et al*., 2024; Spencer *et al*., 2010). The following is a summary table regarding the mechanical properties.

Table 1: Mechanical properties of adhesive systems

PROPERTIES	DESCRIPTION
TENSILE STRENGTH	The ability of a material to resist the force that tends to pull it in opposite directions. In the context of adhesive systems, this refers to the maximum force that the adhesive interface can withstand before it fails due to tensile. This property is commonly measured by tensile tests, where a sample of adhesive is stretched to failure. The results are expressed in megapascals (MPa). A high tensile strength is critical to ensure that the bond between the restoration and the tooth structure remains intact during occlusal forces such as chewing. This is especially important in posterior tooth restorations, where the forces can be significant.
SHEAR STRENGTH	Adhesive's ability to resist forces that tend to slide adhesive surfaces over each other. This strength is critical in situations where restorations are subject to lateral forces. Shear tests are performed by applying a load until the adhesive interface fails. The results are also expressed in MPa. High shear strength is necessary to ensure the durability of restorations, especially in areas such as back teeth that are often subject to chewing forces. An adhesive with poor shear strength can lead to premature failures such as peeling.
FLEXIBILITY	The ability of a material to deform under pressure or stress without breaking. For adhesives, this translates to how they can accommodate forces without causing fracture. It can be evaluated by bending or strain tests, where the amount of strain under a load is measured. The modulus of elasticity can also be calculated. Flexibility is vital in fillings that need to adapt to natural mouth movements. An adhesive that is too rigid can break under pressure, while a flexible adhesive can help distribute forces more evenly, preventing fractures in both the restoration and the tooth.
HARDNESS	Resistance of a material to permanent deformation or scratches. It is an important measurement that indicates resistance to abrasion and wear. It can be measured using scales such as Shore (A or D) or Vickers. The Shore test is particularly useful for adhesives, while the Vickers test is more common for solid materials. Adhesives with adequate hardness help resist the wear and tear that occurs during chewing and cleaning, maintaining the integrity of the restoration. Too low a hardness can result in accelerated wear, while an excessively high hardness can affect the tooth's ability to conform.
MODULUS OF ELASTICITY	It is a measure of the material's stiffness, defining the relationship between the applied stress and the resulting strain. The modulus of elasticity is calculated from compression or tensile tests, where the strain under load is measured. The results are expressed in MPa. An adequate modulus of elasticity is essential for the adhesive to withstand chewing forces without breaking or deforming excessively. Adhesives that are too rigid may not conform well to the dental substrate, while adhesives that are too flexible may not provide the necessary strength.

COEFFICIENT OF THERMAL EXPANSION	It measures the change in volume of a material in response to temperature variations. In adhesive systems, this property is critical for compatibility with dental substrates. The coefficient is often determined through tests that measure the dimensional change of a sample when exposed to temperature variations. A coefficient of thermal expansion that matches that of dental substrates is essential to avoid stresses that could lead to failures at the adhesive interface. Excessive stresses due to thermal expansion differences can result in microcracks, detachment, or restoration failures.
ADHESION TO THE TOOTH SURFACE	Bonding strength between the adhesive and the tooth surface, which can include enamel and dentin. It is influenced by factors such as surface roughness and the presence of moisture. Adhesion is often evaluated through tensile or shear strength tests at the adhesive interface, where the force required to separate surfaces is measured. Effective adhesion is critical to the longevity of the restaurant. A weak union can lead to fading or failure of the restoration, especially in load-bearing areas. Proper preparation of the tooth surface and the use of compatible adhesives are essential to optimize this property.

Source: Authors, 2024

CLASSIFICATION OF ADHESIVE SYSTEMS

Restorative procedures used to be performed by obtaining a cavity based on macro-mechanical retentions that compromised the healthy tooth structure. With the advancement of technology, adhesive systems emerged that significantly revolutionized operative dentistry, as they allowed minimally invasive dental procedures to be performed (Cadenaro *et al*., 2019).

Dental adhesives are composed of low-weight molecules (monomers) that convert into high-weight molecules (polymers) that cause a strong bond between the adhesive layer and the resin composite (Hilton *et al*., 2013; Cadenaro *et al*., 2019). All adhesive systems are resin-based materials capable of allowing the adhesion of restorative materials to enamel and dentin, through a process called copolymerization at the adhesive-compound interface. This process is similar for all adhesive systems (Truffier-Boutry *et al*., 2003; Endo *et al*., 2007; Cadenaro *et al*., 2019).

Dental adhesives were often referred to and categorized into generations, which demonstrated handling technique or advances in formulations rather than new adhesion concepts or mechanisms (Bedran-Russo *et al*., 2017). These practices have led to many complex and confusing classifications that have generated certain difficulties for clinicians in the selection and appropriate use of dental adhesives (Souza-Júnior *et al*., 2010). The adhesive systems used today can be classified into pre-acid or conventional technique, self-etching, and universal systems based on the smear layer, removal, chemical reaction, and the steps involved in their application. However, the selection of which would be the best adhesive approach is still a matter of debate and scientific research (Reis *et al*., 2021; Alsaeed, 2022).

ACID ETCHING

Acid etching is a widely accepted clinical procedure due to its chemical structure and for increasing the useful life of composite resin restorations by decreasing the possibility of marginal pigmentations, secondary carious lesions, and postoperative sensitivity. The effects and results of the acid etching procedure can vary widely, depending on whether the substrate is enamel or dentin (O'Brien, 1998; Yoshikawa *et al*., 1999; Ogata *et al*., 2001; Carvalho *et al*., 2004; Souza-Júnior *et al*., 2010).

Phosphoric acid (typically 35–37%) is the acid conditioner of choice for dental structures, although there are reports in the literature of the use of other acids such as hydrochloric and maleic (Reis *et al*., 2021). In 1955, Michael Buonocore introduced the technique of acid etching in enamel, which remains simple and reliable due to the characteristics of the structure and the performance of the process on it (Pashley *et al*., 2011; Alsaeed, 2022).

The phosphoric acid in enamel increases surface area, surface energy and wettability, which are important physical properties for resin infiltration and the formation of resinous tags after photoactivation, which will trigger the conversion of monomers to polymers. The bond strength is highly stable due to the characteristics of the enamel (high inorganic phase and minimal water content), thus, it can be stated that enamel preconditioning provides the highest enamel bond strength for all contemporary dental adhesives (Luhrs *et al*., 2008; Bedran-Russo *et al*., 2017).

On the other hand, the performance of acid etching on dentin is different from enamel, since they are structures with different compositions. This conditioning promotes the removal of the smear-layer, eliminates the mineral content of the most superficial zone and reduces the hydroxyapatite content in the underlying layers, therefore, the diameter of the dentin tubules dilates, and the dentin permeability and intrapulp pressure increase, exposing the connective tissue that has collagen fibers. These modifications resulting from this acid attack result in a less mineralized, more porous, moist and rough substrate (Reis *et al*., 2021).

PRIMER

The primer penetrates the surface of the demineralized dentin, making it more hydrophobic to receive the application of the adhesive resin (adhesive) on the substrate.

The components of the primer of adhesive systems have hydrophilic monomers and organic solvents in their composition, which aim to increase the wettability and infiltration of the adhesive resin in the dentin substrate (Van Landuyt *et al*., 2007; Hilton *et al*., 2013; Breschi *et al*., 2018; Cadenaro *et al*., 2019).

ADHESIVE RESIN (ADHESIVE)

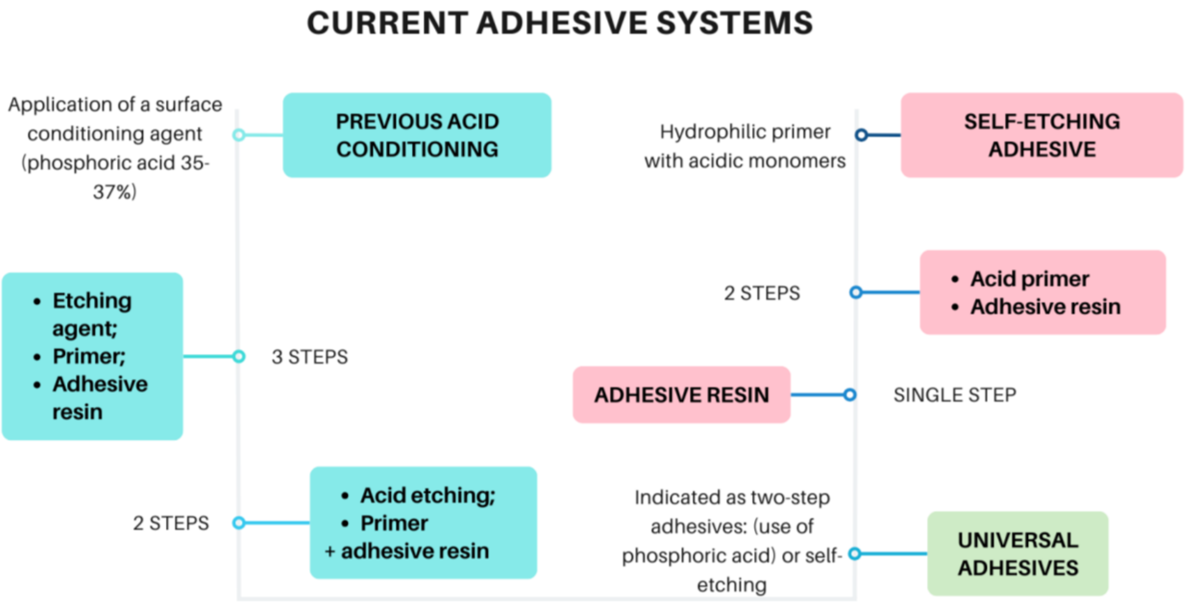
The adhesive is also called a bonding agent, bonding resin or adhesive resin is composed of hydrophobic monomers that penetrate the surface previously demineralized by the acid, creating a micromechanical interaction with the enamel and dentin. This interaction forms the basis of the adhered interface between the tooth structure and the restorative or cementing material, which must have characteristics of insolubility and resistance to degradation resulting from the oral cavity (Swift; Perdigão; Heymann, 1995; Malacarne *et al*., 2006; Liu *et al*., 2011; Hilton *et al*., 2013; Breschi *et al*., 2018; Cadenaro *et al*., 2019).

CURRENT ADHESIVE SYSTEMS

Prior Acid Etching System or Conventional Technique

The adhesion process for pre-conditioning systems (conventional technique) is triggered by the application of a surface conditioning agent (phosphoric acid 35-37%) to eliminate residues from the tooth surface and 17 make it rougher. Soon after, the primer is applied, as it acts as a bifunctional agent and has the function of increasing the fixation between the substrate and the restorative material (Peumans *et al*., 2010; Alsaeed, 2022). Finally, adhesive resin (composed of a monomer, photoinitiator, and fillers) is used. Depending on their type (self-healing, photocuring, or double curing), patches may need to be photocured (Alsaeed, 2022). Figure 2 shows the current classification of adhesive systems.

Figure 2: Contemporary adhesive systems



Source: Authors, 2024.

3-step pre-acid conditioning system (conventional technique):

The pre-acid etching systems (conventional technique) contain three components (etching agent, primer and adhesive resin), packaged in individual bottles and applied in sequence to enamel and dentin. They are considered the gold standard due to their high durability and superior bonding strength, which can reach up to 51.39 MPa (Armstrong *et al*., 2003; De Munck *et al*., 2005; Alsaeed, 2022).

Because of its organic composition, the bond to dentin is more challenging compared to enamel. In addition, during the acid etching process, there is a risk of dentin demineralization, which results in the exposure of collagen fibers or collagen proteins (such as MMP matrix metalloproteinases) that induce the degradation of the hybrid (enzymatic) layer (Alsaeed, 2022).

This consists sequentially of the following steps:

1. Application of acid etching agent
2. Primer Application
3. Adhesive resin (adhesive) application

2-step pre-acid conditioning system (conventional technique):

In the two-step system, the acid etching is done, followed by the application of the primer and adhesive resin (adhesive), however, the primer and adhesive resin are in the same bottle. It is often used in clinical practice to minimize the number of steps in the restorative procedure. However, despite the benefit in relation to the probable reduction in clinical time, the binding strength achieved by this system is weaker compared to the previous system (3 steps), and has greater degradation over time because they are more hydrophilic compared to the 3-step full attack system, which has long-term clinical implications (Armstrong *et al.*, 2003; Alsaeed, 2022).

1. Application of acid etching
2. Application of primer and adhesive resin (adhesive)

Self-conditioning Adesive System

Dental adhesive technology has evolved over the past few decades toward complex formulations with more streamlined clinical procedures. The demand for reduced technical sensitivity, shorter clinical time, and lower incidence of postoperative sensitivity have made self-etching adhesive systems a promising approach when compared to prior acid etching systems (conventional technique) (Van Meerbeek *et al*., 2003; Perdigão; Geraldeli; Hodges, 2003; Giannini *et al*., 2015).

To simplify the one-step adhesion procedure, the adhesive solution has become more hydrophilic due to the increased concentration of acid monomer. However, the increase in the concentration of this monomer compromises the resin bond to dentin, since a semipermeable hybridization is formed. A hybrid layer that is more permeable to water ends up compromising the dentin seal, which results in the premature degradation of the bonds and consequently of the restoration (Tay; Pashley, 2001; Sá *et al*., 2012; Giannini *et al*., 2015)

Current self-etching adhesive systems are divided based on the number of clinical application steps: two-step or one-step adhesives:

Self-Etching Adhesive System (2 steps)

Two-step self-etching adhesive systems include the use of an acid and a hydrophilic primer, which combines acidic monomers that attack and prepare the tooth substrate simultaneously and after the solvent evaporates, a layer of hydrophobic and bonding agent seals the dentin. In short, there is a bottle that includes the acid and the primer, and another bottle that holds the adhesive resin (adhesive) separately (Chigira et al., 1994; Watanabe; Nakabayashi; Pashley, 1994; Tay; Pashley, 2001, Giannini et al., 2015).

1. Acid and primer application
2. Application of adhesive resin (adhesive)

Self-Etching Adhesive System (1 step)

One-step self-etching adhesive systems are all-in-one adhesives, which combine acid, primer, and adhesive resin in the same bottle (De Munck *et al*., 2005; Giannini *et al*., 2015). This contains acidic functional monomers, hydrophilic and hydrophobic monomers, water, and organic solvents in a single substance (Wang; Spencer, 2004; Giannini *et al*., 2015).

1. Application of the acid, primer and adhesive resin (all in the same bottle).

Universal Adhesive Systems

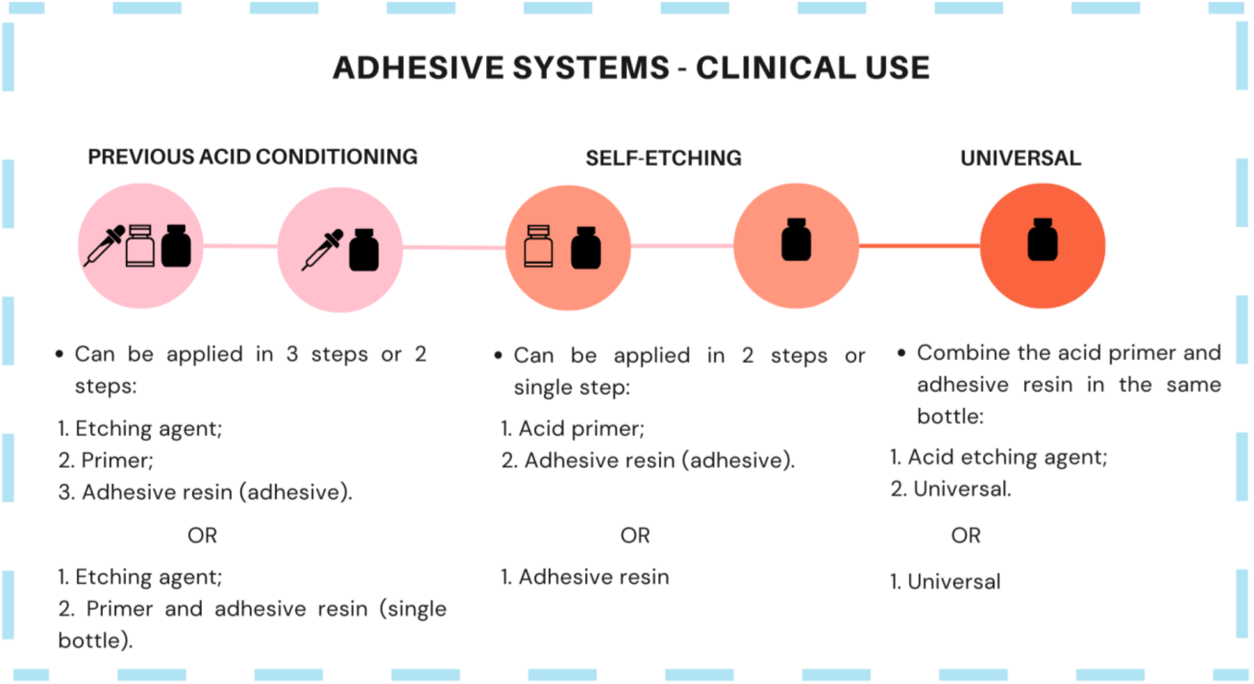
Universal adhesive systems, known as "multimode" or "multipurpose", represent the most common adhesives on the market. This adhesive has in its composition, a 10-methacryloyloxydecyl dihydrogen phosphate phosphate (MDP) that stimulates a solid adhesion to the tooth surface by forming a non-soluble Ca2 salt. This system has dipentaerythritol penta-acrylate phosphate ester and polyalkenoic acid, which are important in chemical bonding to the resinous material (Tay; Pashley, 2001; Alsaeed, 2022).

This proposal aims to simplify the use of this material, as they are single-step. They can be indicated by the respective manufacturers as two-step adhesives: when phosphoric acid is used to pre-condition the enamel and dentin (conventional technique) or self-etching. Clinicians can also use these patches with selective enamel etching, a conditioning technique in which only the enamel is etched with phosphoric acid (Hanabusa *et al*., 2012; Perdigão; Loguercio, 2014; Avelar *et al*., 2019).

1. Application of the acid, primer and adhesive resin (all in the same bottle).

The following flowchart presents the adhesive systems classified according to the composition presented above and their respective clinical uses.

Flowchart 1: Classification of contemporary adhesive systems



ADHESIVE SYSTEMS - CLINICAL USE

PREVIOUS ACID CONDITIONING

- Can be applied in 3 steps or 2 steps:

1. Etching agent;
2. Primer;
3. Adhesive resin (adhesive).

OR

1. Etching agent;
2. Primer and adhesive resin (single bottle).

SELF-ETCHING

- Can be applied in 2 steps or single step:

1. Acid primer;
2. Adhesive resin (adhesive).

OR

1. Adhesive resin

UNIVERSAL

- Combine the acid primer and adhesive resin in the same bottle:

1. Acid etching agent;
2. Universal.

OR

1. Universal

Source: Authors, 2024.

CONCLUSION AND CLINICAL RELEVANCE

Advances in the science of adhesive systems represent a milestone in restorative dentistry, improving the predictability and durability of restorations. The analysis of the history of adhesive systems highlights the technological evolution that has transformed clinical practices. The complexity of tooth structure, with the differences between enamel and dentin, requires specific approaches to optimize adhesion.

The study of the chemical interactions between adhesive systems and dental substrates is essential to improve clinical outcomes. The components of adhesive systems, such as monomers and solvents, are crucial to the performance of the material, influenced by its physical and mechanical properties. The classification of adhesive systems, based on criteria such as the number of application steps, guides the selection of the most appropriate material for each clinical situation. Thus, the integration between science and practice promotes the development of increasingly effective adhesives, ensuring long-lasting aesthetic and functional restorations.

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