

TRABAJO DE FIN DE GRADO

Grado en Odontología

ADHESIVE SYSTEM CHOICE IN COMPOSITE RESIN RESTORATIONS BY DENTISTS IN SPAIN

Madrid, curso 2022/2023

Número identificativo: 210

ABSTRACT

Objective: The aim of this research is to know the preference of dental adhesives used by dentists in Spain and to analyse if dentists apply phosphoric acid on the dentin and to explain all types of adhesives system used in for direct restotaions. Material and methods: This research is a cross sectional study. The instrument used in this study was a standardized survey created in Google Forms Inc, California, USA, consisting of 12 questions with only one possible answer. The survey was distributed using social networks among dentists within the whole Spanish territory. **Results**: The results of a survey conducted among dentists in Spain indicate that the 2-step etch and rinse technique is the preferred method for treating enamel caries, with the majority of dentists using this technique. However, when it comes to treating superficial dentin and enamel caries, dentists are divided between using the etch and rinse technique and the selective enamel technique. When the caries is deeper into dentin, the trend is reversed, with more dentists opting for selective etching over total etching. Therefore, the choice of technique depends on the severity and location of the caries, and dentists are using a combination of techniques to effectively treat their patients. Conclusion: Despite evidence of adverse effects, some dentists still use phosphoric acid etching on dentin. However, the selective enamel etching technique with primer and bonding on both surfaces is widely considered the best method for dentin, while etch and rinse remains the preferred method for treating enamel due to its proven effectiveness.

KeyWords: Adhesive, Adhesion, Dentin, Enamel, Self-Etch, Total Etch, Selective etching, Orthophosphoric Acid.

RESUMEN

Introducción: La odontología ha tenido una gran transición a lo largo de los años que involucra diferentes campos, uno de ellos es el de los adhesivos. El objetivo principal de los adhesivos es mantener la estabilidad y lograr una unión perfecta entre la superficie del diente y el composite. Objetivos: Conocer la preferencia de los adhesivos dentales utilizados por los dentistas en España y analizar si los dentistas aplican ácido fosfórico en la dentina y explicar todos los tipos de sistemas adhesivos utilizados en las restauraciones directas. Material y métodos: Esta investigación es un estudio transversal. El instrumento utilizado en este estudio fue una encuesta estandarizada creada en Google Forms Inc, California, EE. UU., que constaba de 12 preguntas con solo una posible respuesta. La encuesta se distribuyó mediante redes sociales entre los dentistas de todo el territorio español. Resultados: Los resultados indican que la técnica de grabado y aclarado en 2 pasos es el método preferido para tratar la caries del esmalte, y que la mayoría de los dentistas utilizan esta técnica. Sin embargo, cuando se trata de caries superficiales de dentina y esmalte, los dentistas están divididos entre utilizar la técnica de grabado y aclarado y la técnica de esmalte selectivo. Cuando la caries es más profunda en la dentina, la tendencia se invierte, y son más los dentistas que optan por el grabado selectivo frente al grabado total. Por lo tanto, la elección de la técnica depende de la gravedad y la localización de la caries, y los dentistas están utilizando una combinación de técnicas para tratar eficazmente a sus pacientes. Conclusión: A pesar de la evidencia de efectos adversos, algunos dentistas aún utilizan el grabado con ácido fosfórico en la dentina. Sin embargo, la técnica selectiva de grabado del esmalte con imprimador y adhesivo en ambas superficies se considera ampliamente el mejor método para la dentina, mientras que el grabado y enjuague sigue siendo el método preferido para tratar el esmalte debido a su efectividad comprobada.

Palabras clave: Adhesivo, Adhesión, Dentina, Esmalte, Autograbado, Grabado Total, Grabado selectivo, Ácido ortofosfórico.

Table of Content

1.	. INTRODUCTION	1
2.	. JUSTIFICATION AND HYPOTHESIS	3
	2.1. Justification	3
	2.2. Nule Hypothesis	3
3.	. OBJECTIVES	4
4.	. THEORETICAL FRAMEWORK	5
	4.1. Adhesion:	5
	4.2 Principle of adhesion:	5
	4.3 Smear-layer:	6
	4.4. Adhesive:	7
	4.5. Tooth anatomy:	7
	4.6. The process of bonding:	8
	4.6.1. Enamel Dentin Bonding:	11
	4.7. Adhesive Generations:	12
	4.8. Types of adhesives:	16
	4.9. Classification by number of steps:	17
5.	. MATERIALS AND METHOD	20
6.	. RESULTS	23
7.	. DISCUSSION	34
8.	. CONCLUSION	37
9.	. BIBLIOGRAPHY	39

1. INTRODUCTION

Throughout the years, the use of variety of dental adhesives has been a subject of extensive research due to the huge diversity of characteristics that each adhesive present. This progress and development in the adhesives sector has led to revolutionary changes and aspects in restorative and preventive dentistry. The main goal of these researches where targeted to reduce the number of steps at chairside when applying adhesive systems (1). Dental adhesives are widely used and in high demand because of two factors: Aesthetic wise composite restoration present huge advantage over their antecedents, and working on a surface that presents adhesive margin is more liable than a non-bonded interface (1). Understanding adhesion principles, using them appropriately and effectively in our profession is crucial. The classification of dental adhesive depends on different characteristics: Smear layer removal mechanism, number of steps needed, and generation. Generation classification created a conflict since going up by generation means a better version which is not the case in our topic (2). The main purpose of dental adhesives is to secure composite fillings or cements, and they should be capable of resisting mechanical pressure and minimizing shrinkage stress from the composite lining. Additionally, an effective adhesive should also prevent any leakage along the edges of the restoration (10). Dental adhesive was first created in 1949 by Dr. Hagger. It was first introduced as material that has as first substrate dentin instead of enamel (3). In 1951, he developed a cavity seal material that was used in conjunction with a chemical material known as (Sevriton). His products were adopted by various researchers and doctors, who worked on developing it until 1955, when Buonocore invented the acid etching technique, which works on modifying the enamel surface to achieve bonding with the filling material used (3). Several years later, the mechanism of operation was explained, stating that phosphoric acid conditioning of the surface causes micro porosities through which resin penetrates and forms prism-like resin tags (3). He proposed a theory in which dentin bonding was possible (4). Furthermore, due to the rapid contraction during the polymerization process of acrylic filler substances. Buonocore's idea had little effect on restorative dentistry at that moment (3). The crucial turning point that ushered in the era of "Adhesive Dentistry" was the arrival of composite materials that exhibited reduced levels of polymerization shrinkage (3).

For restorations to be successful, it is desirable to provide a strong and long-lasting attachment to the tooth. Understanding adhesion principles and using them appropriately and effectively in our profession is crucial. Since the bonding process for enamel and dentin are different, completing this task is challenging.

2. JUSTIFICATION AND HYPOTHESIS

2.1. Justification

Actual dental practice involves composite resin restorations with the usage of dental adhesive systems. Many of dental restorations fail in causing dental sensitivity and detachment of the filling. These situations happen due to the error in using adhesive systems, and dentists must be aware of the dental substrate and cavity extension to apply them. A survey within the Spanish territory was applied in this research, revealing the preference of dentists using adhesive systems related to direct composite restorations when dentin and/or enamel are substrates to adhere the material for filling. Variables analyzed were in preference of adhesive to fill the cavity when superficial and/or deep dentin is exposed in combined cavitation with enamel and relationship of appearance of dental sensitivity depending on the type of adhesive system used.

2.2. Nule Hypothesis

¿Is selective etching on enamel plus the usage of primer and adhesive in dentin and enamel in deep cavities the preference of dentists in Spain?

3. OBJECTIVES

Main objective:

• To examine the preference of dental adhesives used by dentists in Spain.

Secondary objectives:

- To explain all types of adhesives systems used for direct restorations.
- To analyze if dentists apply phosphoric acid on the dentin.

4. THEORETICAL FRAMEWORK

4.1. Adhesion:

Adhesion by concept is the mechanism of holding two objects together, and it is has three different forms: mechanical form which is related to the penetration of one material to the other, it is the result of strong locking when a contact of two rough surfaces happens (5). The physical form which is considered the weakest type, and is basically the adherence of two different structures by two forces which are: Van Der walls and hydrogen forces (5). Lastly we have the chemical form which is reliable on ionic and metallic bonds, chemical adhesion is the fragile and restricted bonding between the atoms of structurally distinct surfaces (5). Adhesion requirements for a perfect dental agent would be to have high bonding strength, and long term stability(6), endure pressures brought on by polymerization shrinkage and chewing power, prevent any types of microleakage, simple to apply on wet surfaces (Wet-bonding) (5).

4.2 Principle of adhesion:

The primary methods by which dental materials such as adhesives, cements, and self-adhesive restoratives adhere to tooth tissue are through surface wetting, microretention (or mechanical interlocking), and chemical interaction (6). It is important to make optimal use of these mechanisms for durable bonding. Adequate surface wetting is crucial for good interfacial contact between the adhesive material and the substrate. This requires the surface tension of the liquid to be less than the free surface energy of the substrate. Contact angle measurements are used to determine surface wetting behavior, with a lower angle indicating better wetting. Self-adhesive materials have a certain viscosity that can make uniform surface spreading difficult. Various factors such as surface roughness, substrate surface energy, bond-promoting effects, surface hydrophilicity/hydrophobicity, and interfacial pores can also affect adhesion (6)

The most probable way of bonding to mineralized tissues such as enamel and dentin is through microretention or micromechanical interlocking. There are two primary approaches to achieve microretention, which are mechanical roughening and chemical etching (6).

Chemical interaction is the closest possible contact between atoms and molecules, and is believed to enhance bond durability. While it doesn't directly increase bond strength, it can prevent the weakening of bonds over time. When targeting chemical interaction, the focus should be on the inorganic HAp component of dentin, with which ionic interaction can occur as part of the (ultra)mild SE bonding mode. Primary chemical bonding with organic tissue components like dentin collagen is difficult and usually relies on secondary weak forces like van der Waals and hydrogen bonding, which provide little resistance to degradation (6).

4.3 Smear-layer:

The smear layer as a concept is known as the debris that spreads on the tooth after the preparation of the cavity, which is responsible of the blockage of the orifices of dentin tubules by the formations of smear plugs that contributes to an 86% dentin permeability reduction. The smear layer consists of collagen and hydroxyapatite (3). In order to obtain a good adhesion to the dentin, it is advised to partially or completely dissolve the smear layer using Orto phosphoric acid (7).

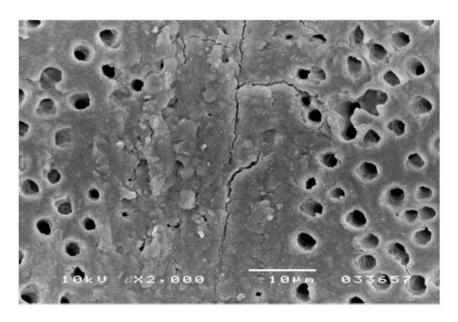


Figure 1: Dentin etched by phosphoric acid (3)

Before the discovery of the phosphoric acid the adhesives used to bond directly to the smear layer, wich was leading to a quick debonding due to the fact that bonding strength was estimated by less than 5 MPa (7). Samples that had de-bonded were categorized as cohesive failure within the smear layer since the adhesive resin, which is hydrophobic and he couldn't pass through such a debris field (8).

4.4. Adhesive:

Resin monomers constitute dental adhesives. They enable resin to interact with dental substrate.(9) Adhesion systems structure present molecules that includes hydrophilic and hydrophobic groups. The first one promotes the ability of the hard tissues to be wetted, while the second one enable interaction and copolymerization with the restorative material (10). Adhesives are composed of other material also such as stabilizers, solvents, curing initiator (10)

4.5. Tooth anatomy:

A tooth mineralized portion is a complicated structure consisting of many hard tissues, each of them has unique ultra-morphology, in addition to a distinct structure. In addition to water and organic material, the hard, crystalline substance hydroxyapatite (Hap) also has a high-energy surface and strong intermolecular forces. In controversy, Dentin structure is composed of HAP that surrounds collagen (3). Inherently moist with less density than enamel, dentin has low intermolecular forces and low-energy surfaces. The main difference that the dentin differs from enamel is the presence of the smear layer, organic materials, in addition to the fluid within the dentinal tubules (3). Smear layer exhibits actual physical barrier behavior which reduce dental permeability by 86% (11). However, the smear layer is porous because of submicron pores that let dentinal fluid flow through them.

Dentin contains numerous tubules or tiny channels that contain fluid. These channels start at the pulp tissue and extend through the dentin, ultimately reaching the boundary between the dentin and enamel. The tubules are twisted and coated with a well-mineralized layer of dentin known as peritubular dentin. In contrast, intertubular dentin is found

between the tubules and is less mineralized than peritubular dentin. The fluid inside the tubules is moved outward from the pulp tissue due to fluid pressure generated by the cells in the pulp, and this movement of fluid can cause tooth sensitivity by stimulating nerve endings in the dentin(5).

Additionally, the density of the tubules is directly related to the with the change in depth being the lowest on the superficial surface increasing going deeper. Due to this morphology the bonding strength of the superficial dentin containing less dentinal tubules come from resin permeating into intratubular dentin, in deeper dentin where the number of dentinal tubules increase the intratabular permeability of resin will result in stronger bonds. Another substrate that ages differently with time is dentin. This asymmetrical physiological aging process causes dentin to become thicker and less permeable (12).

4.6. The process of bonding:

The basic process for bonding to enamel and dentin is basically an exchange process, in which minerals removed from the tooth hard tissues are replaced by resin monomers, which, upon polymerization, become micro-mechanically interlocked in the created porosities (13). The potential benefit of additional chemical interaction between functional monomers and tooth substrate components has recently regained attention, even though the resulting micro-mechanical interlocking is a requirement for good bonding (certainly under clinical circumstances)(14). The primary factor governing how molecules interact with mineralized tissues is usually thought to be an acid's pKa value (15).

Although, it does not completely explain why some molecules attach to it while others do not. For example, 10% maleic acid (pK1 = 1.94, pK2 = 6.23) has a pH of 0.9, while 1 M oxalic acid (pK1 = 1.27, pK2 = 4.28) has a pH of 0.6. However, maleic acid decalcifies hydroxyapatite (HAp), whereas oxalic acid physically binds to it. In other words, it is not always true that solutions will demineralize enamel and dentin to a greater extent the lower the pH (the more acidic) they are (30).

The 'AD-concept' or 'Adhesion-Decalcification concept' describes how chemicals engage with HAp-based tissues (16).

According to this hypothesis, all acids originally chemically (ionically) bond to calcium of HAp (PHASE 1). In order to maintain the surface's electro-neutrality, this initial bonding period coincides with the discharge of phosphate (PO43) and hydroxide (OH) ions from HAp into the own solution. The stability of the formed bond to calcium, or more specifically, the stability of the relevant calcium salt, determines whether the molecule will remain bonded (PHASE 2, OPTION 1 or 2.1) or de-bond (PHASE 2, OPTION 2 or 2.2) (30).

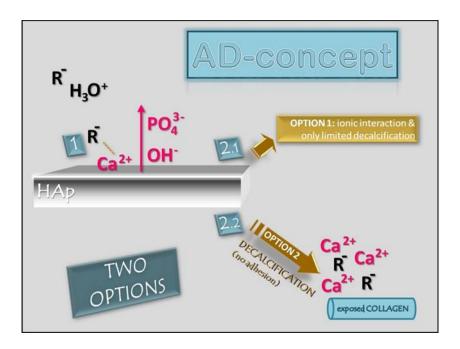


Figure 2: Adhesion Concept

More specifically, molecules like 10-methacryloyloxydecyl dihydrogen phosphate, or 10-MDP, as well as polyalkenoic acids, as functional polymers in glass ionomers, will chemically bond to Ca of HAp (thus according to AD-concept (PHASE 2, OPTION 1 or 2.1), forming stable calcium-phosphate and calcium-carboxylate salts, respectively, with only a minimal surface-decalcification effect. Glass ionomers and "mild" self-etch adhesives do engage with enamel and dentin only briefly and hardly ever dissolve HAp crystals, preferring to retain them in place (within a thin submicron hybrid layer) (30).

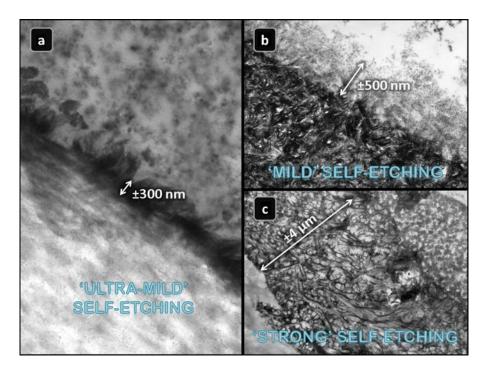


Figure 3: Photomicrographs taken using transmission electron microscopy show dentinadhesive surfaces created by self-etch adhesives, whose ultra-structure relies on how functional monomers interact with the dentin and how acidic the self-etching solution is. A: TEM image of a demineralised and stained section (ultra mild) (30).B: TEM image of a non-demineralised section. The hybrid layer of a 'mild' self-etch adhesive (pH \approx 2) varies between 0.5 and 1 µm (30).C: TEM image of a demineralised and stained section. 'Strong' self-etch adhesives (pH \leq 1) (30).

On the other hand, substances like phosphoric acid and maleic acid, as well as functional monomers of self-etch adhesives like 2-(methacryloyloxyethyl)phenyl hydrogenphosphate (phenyl-P) and HEMA-phosphates, will initially bond to Ca of HAp (PHASE 1), but will easily de-bond (thus according to "AD-concept PHASE 2, OPTION 2 or 2.2"). Depending on the application duration, the positively loaded and consequently electrostatically drawn Ca ions will be removed from the surface to a certain depth by the negatively loaded phosphate ions (or carboxyl groups for carboxyl-based monomers/acids). Since phosphoric acid is commonly used as a "etchant" as part of the "etch-and-rinse" method, this has a harsh decalcification or "etching" impact (30).

4.6.1. Enamel Dentin Bonding:

The process of bonding to enamel is more predictable and did not cause any conflicts around the years as the adhesion to dentin. Diffusion-based micromechanical coupling can be used to explain the basic workings of etch and rinse. The process of "etch and rinse" uses phosphoric acid etching to create deeply etched holes in HAP-rich enamel and demineralize dentin to a depth of 4 to 6 um, revealing a HAp-free collagen network with a sharp transition to the underlying unafflicted dentin. Any surface smudge is entirely eliminated (6).

After the phosphoric acid etchant is rinsed off, enamel can be air-dried, which causes it to become powdered white and serves as a clearly visible indication that the enamel was properly etched. The fact that this enamel etch effect cannot be measured when the etched surface is only blot dried and maintained clearly damp is a drawback (6).

Phosphoric acid on enamel causes large incised holes between the enamel prisms that upon resin implantation, produces tiny resin tags. Individual HAp crystals are thinned at the enamel prism centers by superficial demineralization, and tiny but deeply etched holes are formed into which resin is pulled capillarily to make tiny resin tags. When resin is polymerized, it micromechanically interlocks, creating a strong connection to dental tissue(6). The two steps and three steps etch and rinse proved a similar durability over time (17).

A study made in 2008 showed that enamel margin showed the highest effectivity when enamel was etched with phosphoric acid while it reduced using the self-etch. Overall till our day the etch and rinse is very effective and recommended on the enamel (18).

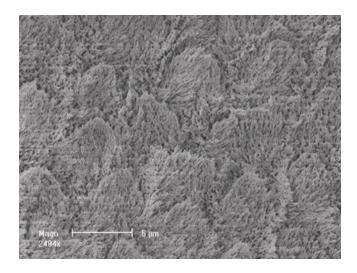


Figure 4: Etched enamel with OP ACID(15)

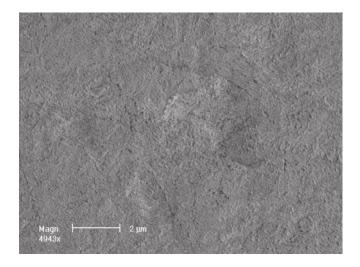


Figure 5:etched enamel with Self Etch(15)

4.7. Adhesive Generations:

The smear layer concept which was causing the blockage of adhesion to dentin was discovered in 1970 by Dr.Eicks, and that is when the concept of total etching was widely spread (19). The coupling agents created in the first generation of bonding systems were to be improved upon in the second generation that came out in the early 1980(3).

Second Generation: This generation improved bonding by including polymerizable phosphates into bis-GMA resins, forming an ionic connection with calcium in the tooth (3). Even though the ionic bonds would quickly deteriorate in the presence of moisture,

frequently leading to debonding or microleakage, despite improvements in coupling agents and a slightly enhanced bond strength of 4 to 6 Mpa (20), these generations were classified as collagen and bonding techniques, they did not manage to achieve good results with thick hybrid layers(6). These sealants actually adhered to the smear layer because the dentin beneath it was only tenuously connected. The marketing of "DENTIN BONDING AGENTS," typical of the era, emphasized the products' specific design and development to bind to the difficult dentin base while enamel bonding proceeded: acid etching was already thought to be effective (6).

Third Generation:

Following Dr. Eick's discovery, the third generation late 1970 early 1980 (9), which was introduced by Fusayama (6), of dental adhesives made it a priority to eliminate or change the smear layer. In an effort to partially dissolve or disturb the smear layer, these new bonding techniques incorporated the procedure of acid etching of the dentin. Acid etching was used to break open the dentin tubules, making it easier to remove the smear layer's particles. A primer might be used after the acid had been removed by rinsing. The dentin and enamel were both then covered with an unfilled resin. While this procedure produced a stronger bond of 12 to 15 Mpa, many physicians believed that dentin shouldn't be etched. On both the dentin and the enamel, an unfilled resin was applied after the primer (9). The MDP molecules were introduced in this generation and they are considered till our days are considered one of the best effective functional monomers (6), by applying this technique in dentin used to deteriorate all hap particles in dentin (6).

Tao et al. in 1988, stated that the unfilled resins in this generation were the weak link since they couldn't successfully penetrate the smear layer. It was the first generation in which adhesives adhered (weakly) to dental metals and ceramics in addition to tooth structure (21).

Dentine adhesion experienced its biggest advancement in the 1990s. With the advent of maleic acid or lower amounts of phosphoric acid, different priming agents, and subsequently the mix of the priming agents and adhesives, dentine etching techniques were

altered. Due to the difficulty in detecting the scratched enamel surface, the less effective acid etch based methods did not last very long and lost favor with practitioners (27).

Fouth Generation:

The fourth generation (1980,1990) was the first generation to be able to remove the entire smear layer. Each component came in a separate bottle (Etchant, primer, bonding) (3), introduced also by Fuyasama (6), the theme of bonding agent was replaced by adhesive systems (6).

This technique consisted on etching both enamel and dentin with phosphoric acid up to 15 seconds (22). To prevent collagen breakdown, the surface must be kept humid ("wet bonding") (3). The exposed collagen network can be penetrated by the application of a hydrophilic priming solution, creating the hybrid layer (14). In comparison to previous systems, these adhesives' bond strengths were in the low- to mid-20 MPa range, and they greatly decreased margin leakage (3). It has been referred as the golden generation on which the other generations will be judged (3).

Fifth Generation:

The main goal of the fifth generation (1990) was to reduce the number of steps used in the fourth generation because one they are time-consuming thus increase the margin of error, and second to address the post-sensitivity and collagen collapse issues. It contained both the primer and the adhesive in a single bottle it is known as the 2 step etch and rinse technique (23). These binding systems could be more prone to deterioration by water over time than the fourth generation. This is due to the hydrophilic character of the polymerized primer used in the "one bottle system"(3). The hydrophilic primer is coated by a more hydrophobic adhesive when using the fourth iteration, lessening its susceptibility to water absorption. Not all fifth generation adhesives can be used with core components that are dual- or self-cured. The tertiary amine in chemical-cured composites is deactivated because the Oxygen-inhibited layer has a lower PH than the surrounding material or because the monomers in some streamlined products are too acidic. It is crucial to follow the manufacturer's instructions because both the quantity of applications (unfilled need more applications) and the number of applications are the same (3).

Sixth Generation:

The sixth generation (1990, 2000) made a new perspective in dentistry and its main goal was to eliminate the etching process or add it to another step (self-etching primer + adhesive) or (self-etching adhesive),(3). Despite having a strong bind to dentin, sixth-generation adhesives' adhesion to enamel is poorer than that of the two previous generations we related this to reduced ph concentration present in this product.(3) In order to prevent bacterial inflammation of the dentin and pulp tissue of the smear layer as well as to lessen fluid movement in the tubules and dentin permeability, SE adhesive systems have been created.(6)

Therefore, the film layer is not removed but rather is solved in order for SE glue systems to function. These systems minimize the steps of clinical application and save doctors' time because they do not require the roughening with distinct acid, washing, and drying procedures found in ER adhesive systems. This system does not use the wet-bonding process and is not susceptible to variations in dentin moisture (5).

As a solution, it was suggested to etch the enamel with the normal phosphoric acid and use this generation over the dentine only. Sixth-generation items are less popular than those from earlier generations since initial binding strength substantially decreases with time (3).

Seventh Generation:

The seventh generation (1999-2005) is considered the most simplified generation as it included all the components in one bottle (24). One challenge was maintaining the stability of the solution (14). The ingredients in the adhesive systems are inherently acidic, and are prone to chemical breakdown and hydrolysis because they contain a large amount of water (15). As a result, the adhesive system becomes unstable more quickly than in previous generations. Additionally, they are more hydrophilic than the two-step self-etch systems of the sixth generation and are more prone to moisture absorption (3).

Eighth generation:

Voco America unveiled voco futurabond DC, an eighth-generation bonding agent with nanosized fillers, in 2010(3). The penetration of resin monomers and the thickness of the

hybrid layer are both increased by the addition of nano-fillers, whose average particle size is 12 nm, which enhances the mechanical characteristics of the bonding systems.(25). Longer-lasting nanofillings known as nano-binding agents exhibit improved enamel and dentin binding strength and stress absorption (26).

4.8. Types of adhesives:

Etch and rinse: It comes in a form of two steps or three steps, it is introduced as the types of adhesive that eliminates the smear layer (2). It consists in applying orthophosphoric acid on both enamel and dentin (2). In addition to removing smear layer moreover, the acid removes hydroxyapatite by decalcifying the dentin's top 1–5 mm of dentin (2). After this chemical etching, scratched dentin is infiltrated with a combination of resin monomers (primer/adhesive) mixed in an organic solvent. The solvents have the power to remove water from the dentine surface, whilst monomers are in charge of increasing the wettability and encouraging the re-expansion of the collagen network. This prepares the collagen network for the following penetration of adhesive resin (27). The resin-dentin interdiffusion zone, also known as the hybrid layer, is the consequence of this infiltration and is made up of collagen, resin, leftover hydroxyapatite, and minute amounts of water(5). This along with the resin tags present inside the dentine tubules provide the composite restoration micromechanical retention (28). The two step technique emerged from the three step technique and consisted on having the acid and primer mixed in one bottle followed by the adhesive in a different bottle.

<u>Self Etch:</u> Self-etching systems were developed to manage the etch-and-rinse technique's sensitivity to humidity as well as to streamline clinical processes for applying adhesives, shortening the length of time spent in the clinic.(29) Self-etch (SE) adhesives are substances that adhere without the need for a separate etching procedure. The smear layer is not eliminated by their non-rinsing acidic primer. Instead, it gently decalcifies the surface hydroxyapatite in dentin while integrating the smear layer residues into the adhesive contact (2). The acidity of the primer—ultra-mild (pH 2.5), mild (pH 2), or intermediately strong (1-2) or strong (<1) determines the degree of decalcification (2). It comes in form of

two or one step (2). The single bottle includes all hydrophilic, hydrophobic and acidic monomers plus water and solvents and resin component and photo-inhibators (3). To ensure the ionization of the acidic functional monomers in single-step self-etch adhesives, water must be used as the solvent. Organic solvents are then added to help blend the hydrophilic and hydrophobic components (30).

<u>Universal adhesives:</u> One of the most recent advancements in adhesive dentistry was the development of universal adhesives, which have been in use in clinical settings since 2011. Since 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 process known as "selective enamel etching"), these new products are known as "multi-mode" or "multi-purpose" adhesives (31). The assertion that UAs may be utilized with any adhesive approach is not supported by the available laboratory and clinical evidence. The durability of this binding is material-dependent and susceptible to hydrolytic breakdown, despite the fact that they may chemically connect to a variety of tooth and direct/indirect restorative substrates. As a result, further steps are still required to guarantee long-term durability. It calls into question UAs' adaptability (32).

4.9. Classification by number of steps:

- Three steps: Includes Etch, primer, Bond (3)
- Two steps: Includes etch, Primer and bonding in a single bottle(3)
- Two steps: Etch and prime in a bottle, and bond in other(3)
- One step: All in one bottle includes self -etch and bonding (3)

Etchant: Composed of orthophosphoric acid of 37% used to prepare the surfaces of dentin and enamel to receive the adhesive. Its main action refers in creating microporosities .This contributes to the development of the resin tag and ultimately leads to micromechanical bonding (3).

Primer: the primer is made up of hydrophilic monomers often transported in a water-soluble solvent In order to encourage excellent flow and penetration into hydrophilic dentin, which might affect the resultant bond strength (3).

Dentin adhesive: can be characterized as a thin, often empty layer of resin placed in between a composite's conditioned dentin and resin matrix. The resin cement or resin composite restorative material adheres to enamel or dentin more effectively thanks to the adhesive. The hydrophilic resin primer and the hydrophobic resin composite are connected by adhesives (3).

Filler: Added in the 8th generation, fillers regulate handling and might boost strength. The film thickness of the adhesive layer may be increased by fillers.

Solvents: Such as ethanol, acetone, water. The rate of evaporation in the mouth and on the tray is influenced by the solvent.

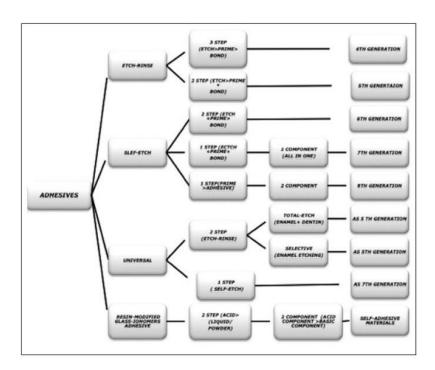


Figure 6: Adhesive Generations (3)

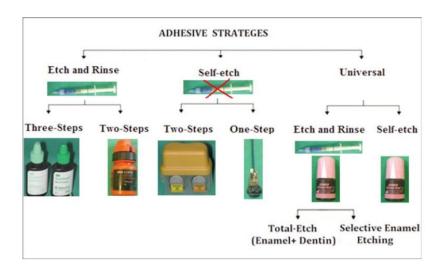


Figure 7: Adhesive strategies(3)

5. MATERIALS AND METHOD

This research is a cross sectional study. The instrument used in this study was a standardized survey created in Google Forms Inc, California, USA, consisting of 12 questions with only one possible answer. The questionnaire was approved by the Ethic Committee of the Universidad Europea the 30th of January 2023, CIPI/23.019. The survey was distributed using social networks among dentists within the whole Spanish territory. **Table 1** shows the applied survey.

Collected data was statistically analyzed using MICROSOFT EXCEL (EEUU) and variables were preference of adhesive to fill the cavity when superficial and/or deep dentin is exposed in combined cavitation with enamel and relationship of appearance of dental sensitivity depending on the type of adhesive system used.

Table 1. Survey applied in the study.

ENCUESTA

CONSENTIMIENTO INFORMADO

El presente cuestionario forma parte del Trabajo de Fin de Grado en Odontología de la Universidad Europea de Madrid, en la titulación de **inglés**, con el título: "Adhesive system choice in composite resin restorations by dentists in Spain" y en **español**: "Preferencia del sistema adhesivo en las restauraciones de resina compuesta por los dentistas en España", dirigido por el Doctor Gerardo José Joves Méndez. El propósito del presente trabajo es saber cuál es el sistema de adhesivo de preferencia usado en restauraciones directas con resina compuesta según el caso y la información será recogida a través de una breve encuesta.

Su participación en este estudio es de carácter libre y voluntario, pudiendo solicitar ser excluido del mismo, sin justificación previa ni perjuicio para usted. La información recogida será confidencial y no se usará para ningún otro propósito fuera de esta investigación y derivados de la divulgación investigativa. Los datos recogidos serán completamente anónimos. No se solicitarán datos personales identificativos. Los datos que se recojan en la encuesta se tratarán de acuerdo con lo establecido en la Ley Orgánica 3/2018, de 5 de diciembre, de Protección de Datos Personales y garantía de los derechos digitales.

A los efectos de lo dispuesto en el reglamento de la Ley Orgánica 3/2018, de 5 de diciembre, de Protección de Datos Personales y garantía de los derechos digitales, queda informado y es expresamente consiente de la utilización de los datos proporcionados en la encuesta, con los fines anteriormente indicados. El presente consentimiento se otorga sin perjuicio de todos los derechos que le asisten en relación con normativa anteriormente citada, existiendo la posibilidad de acceder a la información proporcionada, rectificación, cancelación y oposición en cualquier momento que lo desee.

	o debe iose.joves@	_	-	escrito al ropea.es).	tutor	Prof.	Doctor	Gerardo	José	Joves	Méndez
resultad	os en la	encuest	a se u	oarticipaci utilicen er de resina (n el Tra	abajo F	in de G	rado: <i>Pre</i>	eferen	cia del	-
2. Géne	o.:										
Hombre Mujer Otro											
3. ¿Dóno	de cursó :	sus estu	dios d	le odonto	logía?						
	idad espa idad extr										
4. ¿Trab	aja actua	lmente	como	dentista	en Esp	aña?					
SI NO											
3. Años	de trabajo	o como d	dentist	ta:							
1 a 3 4 a 6 7 a 9 Más que	e 10										
5. ¿A qu	e dedica l	a mayor	parte	de su prá	ictica d	ental?	Elegir ur	na opción			
Estética Restaura Cirugía Periodo Ortodor	ncia icia pediatría ncia										
6. ¿Está compos		ualizado	en cu	anto a los	sistem	as adh	esivos pa	ira restau	racion	nes dire	ctas con
Si No											

No sabe

7. ¿Qué tipo de sistema adhesivo usa en restauraciones con resina compuesta que involucre sólo esmalte?

Grabado total en 3 pasos: ácido, primer y bonding.

Grabado total en 2 pasos: ácido y bonding. Autograbado en 2 pasos: primer y bonding.

Autograbado de 1 paso: primer y bonding en 1 bottle.

No sabe.

8. ¿Qué tipo de sistema adhesivo usa en restauraciones con resina compuesta que involucre esmalte y dentina superficial?

Grabado selectivo en esmalte, primer y adhesivo en ambos sustratos.

Grabado total en 3 pasos en ambos sustratos.

Grabado total en 2 pasos: ácido y bonding. Autograbado en 2 pasos: primer y bonding.

Autograbado de 1 paso: primer y bonding en 1 bottle.

No sabe.

9. ¿Qué tipo de sistema adhesivo usa en restauraciones con resina compuesta que involucre esmalte y dentina profunda?

Grabado selectivo en esmalte, primer y adhesivo en ambos sustratos.

Grabado total en 3 pasos en ambos sustratos.

Grabado total en 2 pasos: ácido y bonding.

Autograbado en 2 pasos: primer y bonding.

Autograbado de 1 paso: primer y bonding en 1 bottle.

No sabe.

10. ¿Ha tenido pacientes que refieren sensibilidad dental por haber hecho alguna restauración con resina compuesta?

SI

NO

No sabe

11. ¿Cree Usted que el sistema adhesivo usado en la restauración ha sido la causa de la sensibilidad?

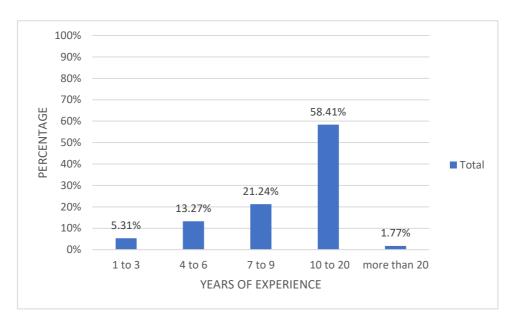
SI

NO

No sabe

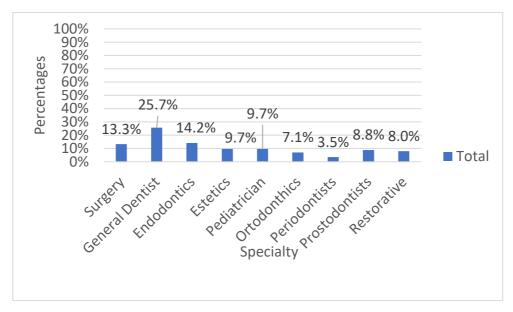
6. RESULTS

A descriptive statistical analysis was applied to data collected from the survey. A hundred and thirteen (113) Doctors around Spain volunteered to participate in the survey, the information was collected in a standardized manner using an online questionnaire composed out of 12 questions. Description of results is shown in the following graphs.



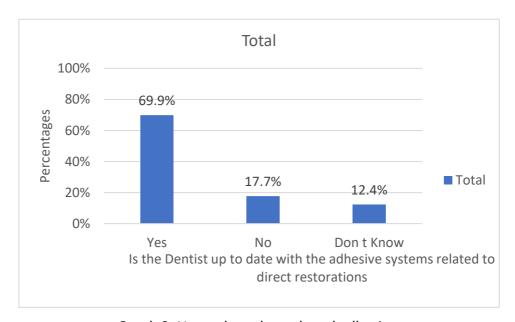
Graph 1. Years of experience

Graph 1 displays the proportion of dental professionals who engaged in the investigation. It reveals that 58.41% most of them had a practice period over 10 years. The least amount of professionals were with a percentage of 1.77.



Graph 2. Specialties

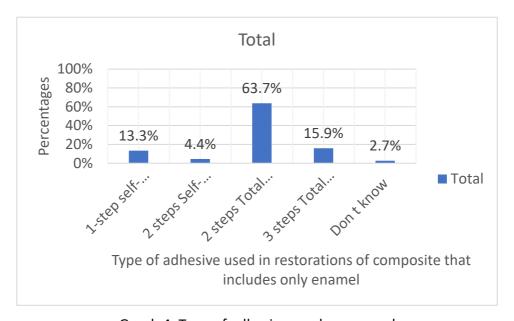
The respondents to the survey were classified according to their dental specialization, with 25.7% identified as general dentists, 14.2% as endodontic specialists, 13.3% as practicing surgery, 9.7% as estheticians, 9.7% as pediatricians, 8.8% as prosthodontists, 7.1% as orthodontists, and only 3.5% as periodontal specialists (**Graph 2**).



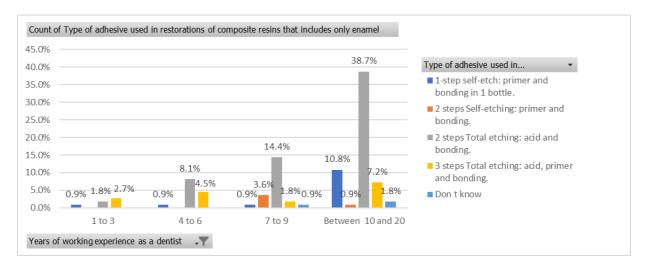
Graph 3. Up-to-date about dental adhesive.

In response to the question that if the Dentist is up to date with the adhesive systems related to direct restorations (**Graph 3**), 69.9% of participants answered yes. After examining the Excel format, it was discovered that all fresh graduates with 1 to 3 years of experience considered themselves up-to-date with adhesive systems. However,

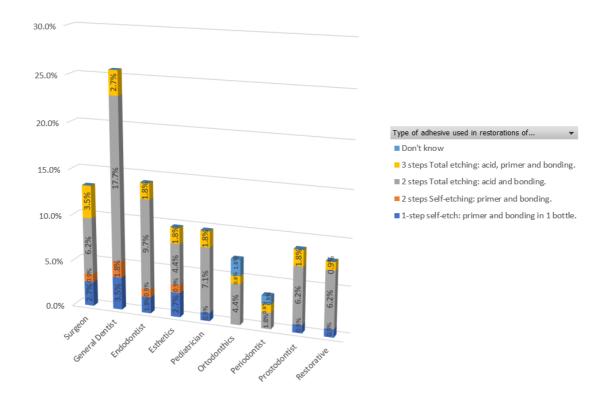
among those with 4 to 6 years of experience, only 0.88% were up-to-date, and 1.77% were unaware of the latest adhesive system inventions. For those with 7 to 9 years of experience, 1.77% were unsure if they were up-to-date, and 6.19% were not up-to-date. Of those with over 10 years of experience (58.41% of the total), 8.85% were unsure if they were up-to-date, and 8.85% were not. As there were only two participants with more than 20 years of experience, we cannot draw a conclusion from their data. Nevertheless, the numbers imply that knowledge of adhesive systems increases with professional years and years since graduation, indicating most dentists stay current with the latest developments.



Graph 4. Type of adhesive used on enamel

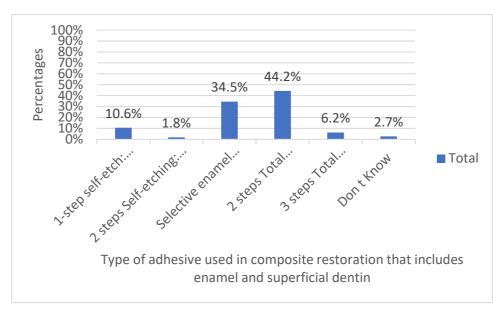


Graph 5. Type of adhesive used on enamel restoration by Dentists according to their years of experience

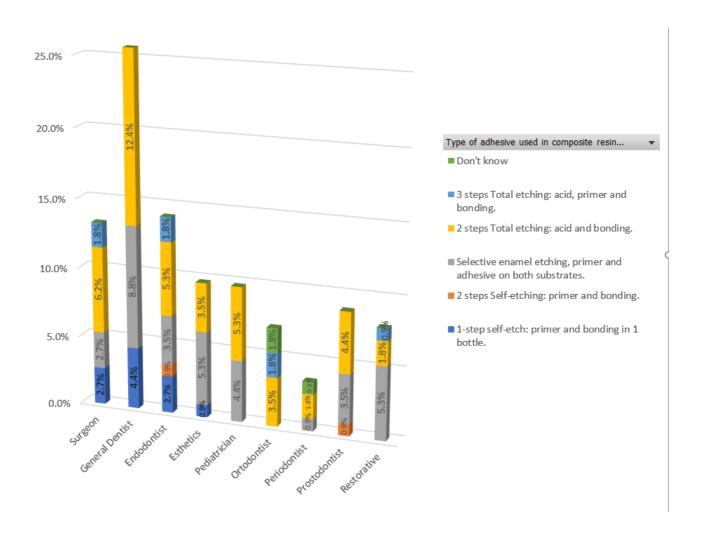


Graph 6. Type of adhesive used on enamel restoration by Dentists according to their specialty.

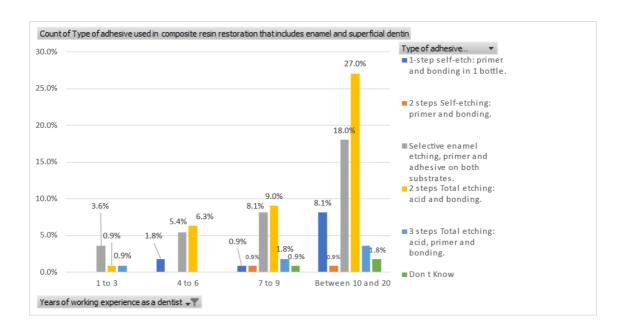
Regarding the type of adhesive used on enamel (**Graph 4**), it became evident that 63.7% of respondents use the two-step total etch technique that involves both acid and bonding, while 15.9% use the three-step version of the same technique that requires an additional bottle. Furthermore, 13.3% use the one-bottle self-etch technique, with the majority having over 10 years of experience, which may indicate a lack of up-to-date knowledge or outdated training. Some dentists use a variant of the total etch technique that combines the acid and primer in one bottle, with bonding in a separate bottle. This percentage is divided amongst those with seven or more years of experience. Finally, 2.7% of participants were unsure of the type of adhesive they were using, with this percentage also divided between those with 7-10 years of experience and those with over a decade of experience (**Graph 5**). When comparing the specialties of dentists, those in endodontics and restorative dentistry, who accounted for 14.1% and 7.9% of participants, respectively, mostly agreed on using the total etch technique. Only 2 out of 16 endodontic specialists (3%) and 2 out of 7 restorative dentists (1.7%) used a different technique (**Graph 6**).



Graph 7. Adhesive used on enamel and superficial dentin

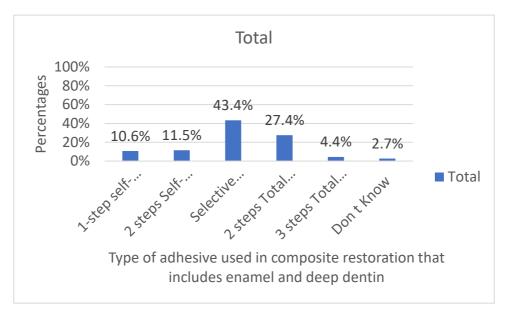


Graph 8. Type of adhesive used on enamel restoration by Dentists according to specialties.

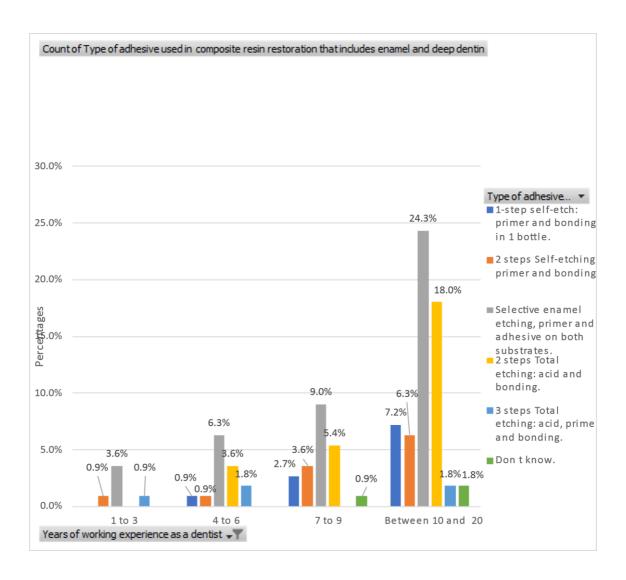


Graph 9. Type of adhesive used on enamel and superficial dentin restoration by Dentists according to their years of experience.

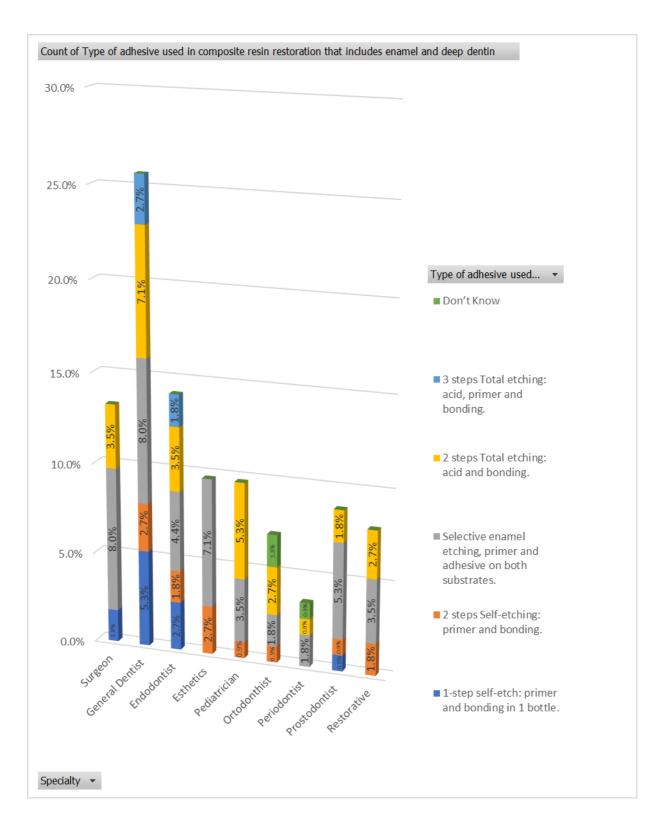
With regard to the type of adhesive used on enamel and superficial dentin (Graph 7), 44.2% of participants reported using the two-step total etch technique. Of these, 26.55% had over 10 years of experience. Additionally, 6.19% used the three-step total etch technique, with 3.54% having more than 10 years of experience. 34.5% used the selective enamel etching technique, with a high percentage of these participants also having more than 10 years of experience. 10.6% reported using the one-step self-etch technique, with 1.77% using the two-step self-etch technique. The variation in responses may be due to differences in knowledge, as mentioned earlier, where some participants tend to follow less as they gain more experience. Others may struggle to keep up with the latest inventions in their field, and some respondents may be influenced by their dental education. The 2.65% who were unsure which adhesive type they used on tooth structures had the same response to the previous question. When examining results by specialty (Graph 8), restorative dentists mostly used selective enamel etching techniques, while other specialties varied between techniques. For example, among endodontic specialists, 3.54% reported using selective enamel etching, 5.31% used the two-step total etch technique, 1.77% used the three-step total etch technique, and 0.88% used the two-step self-etch technique. Dental professionals who completed their education in Spain or abroad reported the same percentage of using the two-step total etch technique, followed by selective enamel etching and one-step self-etch techniques.



Graph 10. Adhesive used on enamel and deep dentin



Graph 11.Type of adhesive used on enamel and deep dentin restoration by Dentists according to their years of experience.

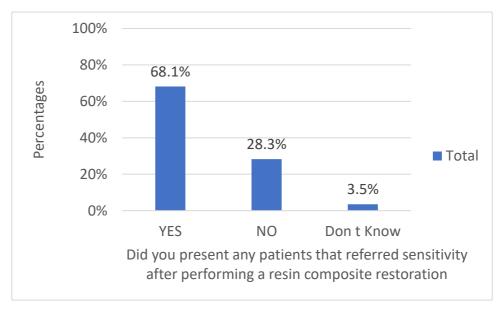


Graph 12.Type of adhesive used on enamel and deep dentin restoration by Dentists according to their years of experience.

When asked about type of adhesive used for enamel and deep dentin restoration (**Graph 10**), 43.4% responded that the technique used is selective enamel etching out of these

23.89% have an experience of over 10 years, 8.85% worked between 7 and 9 years, and it can be seen that the majority of fresh graduates except for 1 person uses this technique. None of the specialties in concrete dominated this answer. In second place it can be seen the technique of total etch in 2 steps with a percentage of 27.4% the percentage here increase by the years of experience but in none of them dominates over the selective enamel technique, and the specialists also none of them dominated in this technique surprisingly a small percentage of restorative dentists uses this technique. The self-etch adhesives in two steps had a percentage of 11,.5% different type of specialties uses this technique and dentists with different levels of experience also only one fresh graduate use this technique, for the self-etch 1 step technique 10.62% uses this technique none of these specialists is and restorative dentistry specialist neither esthetics and a small percentage of endodontists do so, the rest do not know which type do they use.

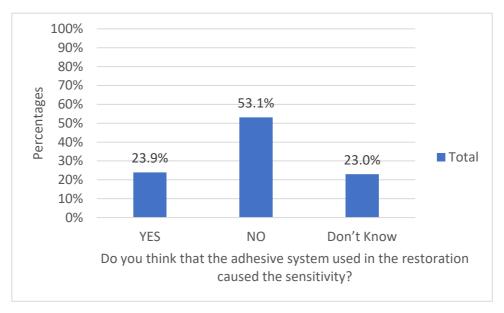
For studying abroad or in Spain mostly, the percentages are the same but the self-etch technique is used by a higher percentage of dentists who graduated in Spain.



Graph 13. Sensitivity after composite restoration

Graph 13 shows that most respondents (68.1%) reported experiencing post-restoration sensitivity. This percentage was highest among those who received deep dentin restorations using either the total etch or selective enamel techniques. Sensitivity was mainly observed in situations where caries affected the enamel, superficial dentin or

deep dentin, and was predominantly associated with the total etch technique. Only a small percentage of those who answered yes used the self-etching technique, whether in one or two steps. No specific dental specialty was associated with post-restoration sensitivity. Of those who answered no, representing 28.3% of the total responses, the majority used the selective etch or self-etch techniques in deep restorations. The difference in sensitivity could be patient-dependent and determined by anatomy. A small percentage of respondents were unsure if their patients experienced sensitivity, possibly due to patients not returning for follow-up appointments or dentists working in different clinics without direct contact with their patients.



Graph 14. Adhesive related to sensitivity

When asked if they attributed sensitivity to the adhesive system used (**Graph 14**), 53.1% of respondents answered no, with approximately 40% of those being up-to-date with adhesive system developments. Among general dentists, 20 out of 29 supported this response, while half of the other specialties also answered no. The remaining half of respondents were divided between those who answered yes and those who were unsure if sensitivity was related to adhesive systems.

7. DISCUSSION

As seen before the adhesive systems nowadays are divided into two different groups one is the etch and rinse which presents the three steps technique and the two steps technique. The three steps one includes acid primer and bonding each one in a bottle and the two steps which have reduced the number of steps by including both primer and bonding in a single bottle and acid in another one. The other system which is self-etch technique consists either of two steps hydrophobic resin alone and primer and etching together or one step all components mixed in a bottle (33).

Upon comparing our study with various other studies conducted on the same topic (34), we observed that our study had a higher participation rate of women, with 70% of participants being female and only 30% male. In contrast, in another study, the majority of participants had 1 to 5 years of experience (34), whereas in our study, participants with more than 10 years of experience were the largest group, with a smaller number of fresh graduates. However, both studies had a relatively small number of participants with more than 20 years of experience. We found that a considerable proportion of our participants had experience between 6 and 9 years, while the other study had a majority of participants with 7 to 9 years of experience.

In terms of restorations, the responses varied significantly in both studies. While our study focused on the types of adhesives used in different areas of the tooth, the other study aimed to determine the procedures used for anterior and posterior composite restorations without specifying the affected area of the tooth. Among fresh graduates, we observed a high preference for the etch and rinse technique, with a higher preference for the 2-step technique over the 3-step technique for anterior restorations. However, for posterior teeth, the self-etch technique was more prevalent, with a significant proportion of participants using the all-in-one bottle method along with a notable percentage of etch and rinse.

For dentists with over 10 years of experience, the self-etch technique was dominant for anterior restorations, with a preference for the 1-step technique. For posterior teeth, the etch and rinse technique had a higher percentage of use, with the 2-step technique being the most used, followed closely by the self-etch technique. In our survey, dentists with over 10 years of experience tended to use the etch and rinse technique in high

percentages for enamel caries, with a preference for the 2-step technique. However, when caries exposed both dentin and enamel, the usage of the 2-step etch and rinse technique was the highest. Selective enamel etching also had a high percentage of usage, whereas for deeper dentin exposure, the percentages between selective etching and total etch of 2 steps were almost equal, with a slight preference for the selective etching technique.

In our study variety of methods where used, the etch and rinse in its two systems: the 3 and 2 steps ,with a high preference to the 2 steps since it saves time and easier to use. This technique is highly recommended on enamel and many researches (---) proves it efficacy and durability over time, the problem that we face here that the simplified versions of the adhesives proved to have less durability in terms of bonding, and stability over the years, and this technique with all its efficiency on enamel, the fact of applying phosphoric acid on dentin is a big challenge due to its adverse effect on the dentin structure.

The results of the survey in this study showed a high percentage of dentists that still applies the orthophosphoric acid to dentin being superficial or deep, in superficial dentin 50.4% of dentists uses the Etch and rinse technique, and 31.8% uses this technique in deep dentin.

To achieve better bonding of resin composites, it is recommended to focus on each hard tissue separately. Typically, the etch-and-rinse method is used for enamel, while the 2-step self-etching method is used for dentin, such as in a Class V cavity surrounded entirely by dentin. A clinical study in non-carious Class V cavities found that Clearfil SE Bond Bond (Kuraray Noritake, Japan) had high retention rates and performed well using this approach. However, if phosphoric acid is used to selectively etch enamel margins before applying the self-etching primer, the margins will remain more stable and free of stains over time (34).

Earlier reports have stated that using phosphoric acid for etching dentin unintentionally leads to an inadequate morphology of the hybrid layer when Clearfil SE is utilized (34). The present results strongly support the previously observed micromorphological finding of severe gap formation (35). Importantly, the use of phosphoric acid on dentin

prior to applying either AdheSE or Clearfil SE Bond, two 2-step self-etching adhesives under investigation, led to a reduction of approximately 50% in the marginal quality of dentin following thermomechanical loading(36).

The etch-and-rinse method is regarded as crucial and extremely delicate because overdried dentin prevents the creation of a functionally appropriate hybrid layer by causing demineralized collagen fibers to collapse and minimal monomer diffusion among the fibers (3).

Due to the phosphoric acid aggressivity, the drawback of these systems is that because almost all of the hydroxyapatite has been removed from the dentinal collagen, it is nearly difficult to completely envelop the collagen fibers, which will lead to a location where the binding will weaken over time (26). After washing and drying, the residual collagen fiber network on the dentine surface tends to collapse and diminish as the hydroxyapatite is entirely gone (26) It is more challenging for resin to penetrate all the way to the profundity of demineralization the deeper the dentin is etched, since the phosphoric acid etch the dentin up to 4-5 μ m (6).

It has been established that dentinal collagen revealed by an etch-and-rinse method is extremely susceptible to enzymatic and hydrolytic breakdown processes(35). The use of 40% phosphoric acid to pretreat dentine collagen was found to increase its vulnerability to trypsin digestion compared to collagen that was not treated. The degree of susceptibility was observed to rise as the duration of exposure to the acid increased.(36)

As for the self-etch it was noted that it is no the preferred method used by dentists in Spain a really low percentage of dentists uses this technique, but in the cases where this method was used the dentists preferred the one step self tch on the two steps, linking it to the same reason for which they chose the 2 steps over the 3 steps in etch and rinse also, in Spain we see that the preference of usage in case of dentin exposition is the total etch or the selective etching technique.

Self-etching enamel doesn't create deep micro retentive etching pits, which is why the self-etching effect is inadequate to accomplish lasting bonding to enamel. It also doesn't merely dissolve and thin HAp like phosphoric acid does (6).

Strong self-etch sealants have quite significant impacts on dentin and enamel demineralization. These materials create an interfacial ultra-structure that is similar to that created by etch-and-rinse systems, but varies in that the dissolved calcium phosphates are not removed during the rinse step. In an aqueous setting, these imbedded calcium phosphates are anticipated to be extremely unstable, significantly reducing the interfacial stability (29).

Strong self-etch adhesives typically fail at dentin, according to laboratory and clinical data, despite having a fairly good bonding ability to enamel (37),(38).

In actuality, the capacity of an etch-and-rinse hybrid layer to be demineralized supports the collagen layer's comparatively porous character and potential long-term instability (29). However, it also highlights the significant benefit of moderate self-etch adhesives because they maintain collagen's ability to chemically interact with HAp while keeping collagen encapsulated and thus secured by Hap (14).

After reviewing our results we can accept our null hypothesis after seeing that the majority of dentists in Spain uses the selective etching technique in deep restorations.

8. CONCLUSION

In recent years, there has been much debate over the best technique for adhesion in dentistry. Two popular techniques that have been extensively researched are the selective etching of enamel technique and self-etching of dentin with mild pH. Based on the studies mentioned in the article, it can be concluded that the latter technique is the most effective in terms of adhesion.

The selective etching of enamel technique involves the use of phosphoric acid to etch the enamel surface, creating a rough surface for better adhesion of composite resin. However, research has shown that this technique may not be as effective as previously thought. In fact, many studies have found that self-etching adhesives produce similar or even better bond strength compared to the selective etching of enamel technique.

One advantage of the self-etching of dentin with mild pH technique is that it is less aggressive than the selective etching of enamel technique, which can cause damage to the tooth structure. Additionally, self-etching adhesives eliminate the need for a separate etching step, which can save time and reduce the risk of errors.

Despite the evidence supporting the use of self-etching adhesives, a significant percentage of dentists in Spain still use phosphoric acid to etch dentin. This may be due to a lack of awareness about the latest adhesive systems and techniques. It is important for dental professionals to stay up-to-date with the latest research and developments in the field to ensure the best possible outcomes for their patients.

Another important issue that was discussed in the article is the problem of sensitivity in patients after dental restorations. While sensitivity is a common side effect of many dental procedures, it can be particularly problematic when it comes to adhesives. The sensitivity can be related to various factors such as the adhesive material, the location of the cavity, and the technique used to apply the adhesive.

It is essential for dental professionals to carefully consider all of these factors when choosing an adhesive technique to use in their practice. By selecting the most appropriate technique and material for each individual case, they can minimize the risk of sensitivity and ensure the best possible outcomes for their patients.

In conclusion, the selective etching of enamel technique and self-etching of dentin with mild pH are two popular adhesive techniques used in dentistry. While both techniques have their advantages and disadvantages, the evidence suggests that self-etching adhesives are the most effective in terms of adhesion. However, it is important for dental professionals to stay up-to-date with the latest research and developments in the field to ensure the best possible outcomes for their patients. Additionally, careful consideration of the various factors that can contribute to sensitivity is essential when selecting an adhesive technique for each individual case.

9. BIBLIOGRAPHY

- 1. Dental Adhesives: Past, Present, And Future [Internet]. Oral Health Group. 2019 [cited 2023 Mar 6]. Available from: https://www.oralhealthgroup.com/features/adhesion-past-present-and-future/
- Perdigao J, Araujo E, Ramos RQ, Gomes G, Pizzolotto L. Adhesive Dentistry Current Concepts and Clinical Considerations. J Esthet Restor Dent. 2021 Mar 1;33:51–8.
- 3. Sofan E, Sofan A, Palaia G, Tenore G, Romeo U, Migliau G. Classification review of dental adhesive systems: from the IV generation to the universal type. Ann Stomatol (Roma). 2017 Jul 3;8(1):1–17.
- 4. Swift EJ, Perdigão J, Heymann HO. Bonding to enamel and dentin: a brief history and state of the art, 1995. Quintessence Int Berl Ger 1985. 1995 Feb;26(2):95–110.
- 5. Kazak M, Dönmez N. Development of Dentin Bonding Systems from Past to Present. Bezmialem Sci. 2019 Oct 30;7(4):322–30.
- 6. From Buonocore's Pioneering Acid-Etch Technique to Self-Adhering Restoratives. A Status Perspective of Rapidly Advancing Dental Adhesive Technology. J Adhes Dent. 2020 Feb 14;22(1):7–34.
- 7. Saikaew P, Sattabanasuk V, Harnirattisai C, Chowdhury AFMA, Carvalho R, Sano H. Role of the smear layer in adhesive dentistry and the clinical applications to improve bonding performance. Jpn Dent Sci Rev. 2022 Nov;58:59–66.
- 8. Eick JD. Smear layer--materials surface. Proc Finn Dent Soc Suom Hammaslaakariseuran Toim. 1992;88 Suppl 1:225–42.
- 9. Perdigão J. New Developments in Dental Adhesion. Dent Clin North Am. 2007 Apr 1:51(2):333–57.
- 10. Van Landuyt KL, Snauwaert J, De Munck J, Peumans M, Yoshida Y, Poitevin A, et al. Systematic review of the chemical composition of contemporary dental adhesives. Biomaterials. 2007 Sep;28(26):3757–85.
- 11. Price RB, Dérand T, Andreou P, Murphy D. The effect of two configuration factors, time, and thermal cycling on resin to dentin bond strengths. Biomaterials. 2003 Mar;24(6):1013–21.
- 12. Perdigão J. Dentin bonding-variables related to the clinical situation and the substrate treatment. Dent Mater Off Publ Acad Dent Mater. 2010 Feb;26(2):e24-37.
- 13. Van Meerbeek B, De Munck J, Yoshida Y, Inoue S, Vargas M, Vijay P, et al. Adhesion to enamel and dentin: Current status and future challenges. Oper Dent. 2003;28(3):215–35.

- 14. Yoshida Y, Nagakane K, Fukuda R, Nakayama Y, Okazaki M, Shintani H, et al. Comparative study on adhesive performance of functional monomers. J Dent Res. 2004;83(6):454–8.
- 15. Van Meerbeek B, Yoshihara K, Yoshida Y, Mine A, J. DM, K.l. VL. State of the art of self-etch adhesives. Dent Mater. 2011 Jan 1;27(1):17–28.
- 16. Fu B, Sun X, Qian W, Shen Y, Chen R, Hannig M. Evidence of chemical bonding to hydroxyapatite by phosphoric acid esters. Biomaterials. 2005;26(25):5104–10.
- 17. Peumans M, Kanumilli P, De Munck J, Van Landuyt K, Lambrechts P, Van Meerbeek B. Clinical effectiveness of contemporary adhesives: a systematic review of current clinical trials. Dent Mater Off Publ Acad Dent Mater. 2005 Sep;21(9):864–81.
- 18. Frankenberger R, Lohbauer U, Roggendorf M, Naumann M, Taschner M. Selective enamel etching reconsidered: Better than etch-and-rinse and self-etch? J Adhes Dent. 2008 Nov 1;10:339–44.
- 19. Eick JD, Wilko RA, Anderson CH, Sorensen SE. Scanning electron microscopy of cut tooth surfaces and identification of debris by use of the electron microprobe. J Dent Res. 1970;49(6):Suppl:1359-1368.
- 20. Kugel G, Ferrari M. The science of bonding: from first to sixth generation. J Am Dent Assoc 1939. 2000 Jun;131 Suppl:20S-25S.
- 21. Tao L, Pashely DH, Boyd L. Effect of different types of smear layers on dentin and enamel shear bond strengths. Dent Mater Off Publ Acad Dent Mater. 1988 Aug;4(4):208–16.
- 22. Tay FR, Gwinnett AJ, Pang KM, Wei SH. Structural evidence of a sealed tissue interface with a total-etch wet-bonding technique in vivo. J Dent Res. 1994 Mar;73(3):629–36.
- 23. Freedman G. 7th generation Adhesive Systems Dental Asia (English) March-April 2019. 2019 Mar 1;50–3.
- 24. Alex G. Adhesive Considerations in the Placement of Direct Composite Restorations. In 2007 [cited 2023 Mar 11]. Available from: https://www.semanticscholar.org/paper/Adhesive-Considerations-in-the-Placement-of-Direct-Alex/fae4f9e0658231a161294e50332c1428251ad7c5
- 25. Başaran G, Ozer T, Devecioğlu Kama J. Comparison of a recently developed nanofiller self-etching primer adhesive with other self-etching primers and conventional acid etching. Eur J Orthod. 2009 Jun;31(3):271–5.
- 26. Nair M, Paul J, Kumar S, Chakravarthy Y, Krishna V, Shivaprasad. Comparative evaluation of the bonding efficacy of sixth and seventh generation bonding agents: An In-Vitro study. J Conserv Dent JCD. 2014;17(1):27–30.

- 27. Carvalho RM, Mendonça JS, Santiago SL, Silveira RR, Garcia FCP, Tay FR, et al. Effects of HEMA/solvent combinations on bond strength to dentin. J Dent Res. 2003 Aug;82(8):597–601.
- 28. Van Meerbeek B, Dhem A, Goret-Nicaise M, Braem M, Lambrechts P, VanHerle G. Comparative SEM and TEM examination of the ultrastructure of the resin-dentin interdiffusion zone. J Dent Res. 1993 Feb;72(2):495–501.
- 29. Sundfeld RH, Valentino TA, Sversut de Alexandre R, Fraga Briso AL, Marçal Mazza Sundefeld ML. Hybrid layer thickness and resin tag length of a self-etching adhesive bonded to sound dentin. J Dent. 2005 Sep 1;33(8):675–81.
- 30. Yeniad B, Albayrak AZ, Olcum NC, Avci D. Synthesis and photopolymerizations of new phosphonated monomers for dental applications. J Polym Sci Part Polym Chem. 2008;46(6):2290–9.
- 31. Hanabusa M, Mine A, Kuboki T, Momoi Y, Van Ende A, Van Meerbeek B, et al. Bonding effectiveness of a new "multi-mode" adhesive to enamel and dentine. J Dent. 2012 Jun;40(6):475–84.
- 32. Nagarkar S, Theis-Mahon N, Perdigão J. Universal dental adhesives: Current status, laboratory testing, and clinical performance. J Biomed Mater Res B Appl Biomater. 2019 Aug;107(6):2121–31.
- 33. Burrow M. Understanding adhesive dentistry. Ann R Australas Coll Dent Surg. 2010 Mar;20:75–9.
- 34. Van Landuyt KL, Kanumilli P, De Munck J, Peumans M, Lambrechts P, Van Meerbeek B. Bond strength of a mild self-etch adhesive with and without prior acidetching. J Dent. 2006 Jan 1;34(1):77–85.
- 35. Breschi L, Mazzoni A, Ruggeri A, Cadenaro M, Di Lenarda R, De Stefano Dorigo E. Dental adhesion review: Aging and stability of the bonded interface ScienceDirect [Internet]. 2008 [cited 2023 Mar 29]. Available from: https://www.sciencedirect.com/science/article/abs/pii/S0109564107000541
- 36. Okamoto Y, Heeley J d., Dogon I l., Shintani H. Effects of phosphoric acid and tannic acid on dentine collagen. J Oral Rehabil. 1991;18(6):507–12.
- 37. De Munck J, Shirai K, Yoshida Y, Inoue S, Van Landuyt KL, Lambrechts P, et al. Effect of water storage on the bonding effectiveness of 6 adhesives to class I cavity dentin. Oper Dent. 2006;31(4):456–65.
- 38. Shirai K, De Munck J, Yoshida Y, Inoue S, Lambrechts P, Suzuki K, et al. Effect of cavity configuration and aging on the bonding effectiveness of six adhesives to dentin. Dent Mater. 2005 Feb 1;21(2):110–24.