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Chemical aspects of the dental adhesives.

A literature Review

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Abstract

Adhesive dentistry has undergone significant progress in the last decades. The purpose of this article is to review the literature on the current knowledge of each adhesive system according to their classification. The article emphasises the evolution of dental adhesives and the chemical interaction between their components, the collagen matrix, and hydroxyapatite crystals of the hard dental tissues. It describes the basic strategies of adhesion. The development of adhesives and techniques is a long story. The first generations have low bond strength to the dentin. The third-generation dentin adhesive has better, but not sufficient bond strength. The fourth generation (total-etch) dentin adhesives represent great progress in the dentin adhesives. The evolution of the dentin adhesive continues by simplifying the adhesive protocol (5th -generation), and after that, it is searching for a new strategy for adhesion (6th, 7th and 8th generations self-etching systems).

Keywords: Functional monomers, dental adhesives, chemical adhesion

Introduction

Dental adhesive are solutions of resin monomers that make the resin dental substrate interaction achievable [1]. Adhesive systems are composed of monomers with both hydrophilic groups and hydrophobic groups. Hydrophilic groups bond to the enamel and especially the wet dentin. The hydrophobic groups allow with co-polymerization chemical covalent bond with the composite restorative material [2]. The chemical composition of adhesives also includes curing initiators, inhibitors or stabilizers, solvents and in some cases inorganic fillers [2]. The concept of the etching adhesive is based on the use of the phosphoric acid for removing the smear layer and subsequently it is formed a hybrid layer by using an adhesive monomers. The self-etching adhesives use a acidic monomers that simultaneously condition and prime the dentin and the enamel. Therefore, the self-etching adhesives eliminate the technique-sensitive rinsing step to remove the phosphoric acid from enamel and dentin [3]. However, it is necessary to consider the anatomy of the tooth. Enamel is composed of a hard solid crystalline structure-hydroxyapatite with strong intermolecular forces, high-energy surface. Enamel contains small percent water and organic material. Dentin is a biological composite of hydroxyapatite that envelops collagen. Dentin is intrinsically humid, and less hard than enamel, with low intermolecular forces and low-energy surfaces. The dentin is different from enamel, as it has smear layer, organic contents and presence of fluid inside the dentinal tubules. The enamel can be easily dried, but not the dentin, so bonding process to enamel is different from the dentin [4].

Generation of the dental adhesives

The clinical history of dental adhesives started as early as 1949, when Dr Hagger, a Swiss chemist, applied on a patent for the first time dental adhesive. This adhesive was the commercial product "Cavity Seal". It was combined with the chemically curing resin "Sevriton" in 1951. This product contains glycerophosphoric acid dimethacrylate adhesive, which was polymerized using a sulfinic acid initiator. It is later known as "Sevriton Cavity Seal". This adhesive relies on acidic monomers capable of etching and interacting on a molecular level with tooth surfaces to form physic-chemical bonds between the restoration and the tooth [5]. Other investigators soon adopted Hagger's concept. In 1952, it was postulated by Mclean and Kramer [6] that this material, "Sevriton Cavity Seal", chemically bonded to tooth structures. This investigation was the first report of changes in dentin promoted by an acidic monomer and may be considered a precursor of the hybrid layer concept [6]. In 1956, Bounocore, Brudevold and Wileman [7] evaluated the bond strength of "Sevriton Cavity Seal". They treated cavities with the functional monomer: glycerophosphoric acid dimethacrylate and, after that, applied resin material. This monomer had a pH of 2.5, and the authors felt that the acidity caused some dentin surface dissolution and the tubules' enlargement. According to the authors, this would allow for penetration of the resin into the dentin, causing good mechanical retention. The same investigators based on this thesis used a drop of 7 % hydrochloric acid, and the dentin surface was etched for 1 minute, followed by applying a standard acrylic resin filling material. However, the adhesive properties of this resin are not very good. The adhesive properties of a standard acrylic resin were not increased after the acid treatment. Understanding that the moisture was still a problem and that it inhibited the polymerization process, R. Bowen [mention by Söderholm-8] created in 1962 dimethacrylate by attaching methylmethacrylate to the end groups of the epoxy resin. This change resulted in a new resin called bisphenol A glycidyl methacrylate, or Bis-GMA [8]. Buonocore, Matsui and Gwinnett [9,10] in 1968 made a report on good adhesive bonds with enamel after phosphoric acid conditioning, which produced "prism-like" tags of resin materials (Bis-GMA and UDMA) that penetrated enamel surfaces. However, this conception was unsuccessful in the adhesion to dentin [9,10]. In 1965, R. Bowen [11] developed a coupling epoxy resin agent, N-phenylglycine glycidyl methacrylate (NPG-GMA), which was a bifunctional molecule. A bifunctional molecule can bond to the dentin on one end and composite resin material on the opposite end. Although the bond strength was very low (1 MPa to 3 MPa). It was considered the first generation of dentin adhesives. A breakthrough in adhesive dentistry was introducing the sealant composite system called Nuva-Seal. It had a curing initiator, an ultraviolet light source. Working technique: The teeth were dried, isolated with cotton rolls, and etched with 50% phosphoric acid for 1 minute. The surfaces were then rinsed thoroughly with water, dried, and isolated again. The sealant was applied and then exposed to ultraviolet light for 30 seconds [10]. Although acid etching was used with pit-and-fissure sealants, its routine use in restorative dentistry was still not fully accepted in the 70s of the 20th century. [10]. In their study at the end of 1970s years, Brannstrom and Nordenvall [12] concluded that there was not advantage to etching the dentinal wall of the cavity preparation. An improved cavo-surface marginal seal could be accomplished by only applying an acid gel to the enamel walls. The first system that was considered a new generation of dentin adhesives (2nd generation) is Clearfil™ Bond System F [13]. It contains the functional monomers phenyl-P and HEMA; the solvent is ethanol. This generation of dentin adhesive is based on chemical interaction. Negative charged phosphate groups of the acid ester interact with Ca^{2+} in the smear layer [14]. This generation of dentin adhesives contains functional monomers, which have acid groups for forming ionic bonds with Ca^{2+} from the smear layer and groups for forming a covalent bond with hydroxyl and amino groups of the collagen molecules. However, the chemical adhesion was not satisfactory; bond strength with the dentin was around 5-6 MPa [15]. Therefore, it was concluded that chemical adhesion is not a major part of the good adhesive bond with dentin. It is important for the good sealing of the restoration. In the early 1980s, the prevailing attitude towards bonding to dentin was that the bond strength was poor, and possible sensitivity problems could occur if the dentin were acid etched [16]. Because of this, the next generation (3rd) of dentin adhesives focused on the strategy of modifying the smear layer. The smear layer was either modified or removed without disturbing the smear plugs of the dentin tubules [17]. The bonding systems comprised three parts: conditioner, primer and adhesive. The conditioner consisted of weak organic acid (maleic acid) or a low phosphoric acid concentration that partially dissolved the smear layer [18]. At that generation, adhesives bonding agents to dentin were developed – primers, which contained hydrophilic monomers dissolved in acetone or ethanol and they transformed the dentin surface from hydrophilic to hydrophobic, and primers prepared the dentin surface to bond with adhesive [15]. They have a long hydrophobic part of the molecule for a chemical covalent bond with the adhesive (co-polymerization) and a short hydrophilic part of the molecule for an adhesive bond with the dentin (micro-mechanical and chemical) [15]. The bond strength of the third-generation dentin adhesives is between 8 -15 MPa [17]. Although in the early 1980s, the prevailing attitude was to not etch the dentin, in 1980, Fusayama [mention by Vaidyanathan 16] advocated the etching of dentin to improve overall adhesion. Two years later, Nakabayashi et al.[19] published their report on the safety and improved adhesion of exposing the dentinal tubules through acid etching. He used a 10% citric acid to etch the dentin and applied monomers with hydrophobic and hydrophilic groups. This combination resulted in a bond strength of 18 MPa [19]. In 1985, Nakabayashi [20] described forming a hybrid layer on the dentin surface after its acid etching. Moreover, he demonstrated that resin could infiltrate into acid-etched dentin to form a new structure composed of a resin matrix reinforced by collagen fibrils [9]. Nakabayashi [mention by Inokoshi -21] considered that forming a hybrid layer is the main bonding mechanism of bonding agents. The hybrid layer was best observed by transmission electron microscopy but was later demonstrated by scanning electron microscopy [21]. In the second half of the 1980s and early 1990s, the introduction of three-step total-etch adhesive (4-generation dentin adhesive) represented great progress in adhesive dentistry. The bond strength reaches average 25 MPa and it was significant reduced marginal leakage in comparison with earlier generation dentin adhesives [22]. In this generation, the three primary components are typically packaged in separate containers and applied sequentially – conditioner, primer, and bonding agent. The primer transforms the hydrophilic dentin surface into a hydrophobic sponge, and the adhesive resin (bonding agent) completes the process of hybridisation [9, 15]. Despite the great progress of fourth-generation dentin adhesives, postoperative complaints ranged from cold sensitivity to discomfort with chewing after acid etching the dentin [10]. Kanca [23] discovered that keeping the dentin moist after the etching step improved bond strength while the postoperative sensitivity decreased. Gwinnett [24] and Sugizaki [25] simultaneously published independent studies with similar conclusions. This technique, called "wet bonding, " gave rise to the 4th generation of dentin adhesives [26]. A problem with the wet-bonding technique was that it was difficult to quantify the amount of "wetness" left on the etched dentin surface. After the etching step was completed, a demineralised collagen meshwork remained. One of the roles of the primer was to push the water out from the collagen meshwork; however, if some of the water remained, then phase changes occurred with the adhesive components, resulting in lower bond strengths and postoperative sensitivity. This drawback made the technique's sensitivity highly precise [26, 27]. The fifth-generation dentin adhesives were introduced into practice in the second half of the 90s of the 20th century and the next decade. The aim is to simplify the process of fourth-generation adhesion by reducing the clinical steps. They are indicated as single-step systems with total-etch "one bottle" adhesive. In this generation, the technique of wet bonding has improved, as well as reduced postoperative sensitivity [28, 29]. The adhesion of the 5th generation dentin adhesive to the etched dentin is the same as the fourth generation; it forms a zone of hybridization. The bond strength is 25 MPa [30]. The sixth-generation bonding systems were introduced in the latter part of the 1990s and the early 2000s, also known as "self-etching primers", were a dramatic leap forward in adhesive technology. This generation of adhesives is created to eliminate the acid etching of the dentin with phosphoric acid, as it was in the previous two generations of adhesives. The systems have two components (two bottles): self-etching primer and adhesive [31]. The biggest advantage of the sixth generation is that their efficacy appears to be less dependent on the hydration state of the dentin than the total-etch systems [30]. The self-etching primer performs surface demineralization of the normal dentin as it is dissolved in the smear layer. It is accomplished penetration and infiltration of the hydrophilic monomers. The dentin surface is not rinsed after treatment with the self-etching primer, in that way, there is no loss of wetness from the dentin. In that way, there is a reduced possibility of the collapse of the collagen meshwork [32]. Unfortunately, the first evaluations of these new systems showed a sufficient bond to dentin while the bond with enamel was less effective. According to the investigators, this may be because the acid monomers do not have a sufficiently low pH compared to phosphoric acid [33]. In order to overcome this problem, it is recommended to etch the enamel first with the traditional phosphoric acid before using it. However, those utilising this technique should take care to confine the phosphoric acid solely to the enamel. Additional etching of the dentin with phosphoric acid could create an "over-etch" situation where the demineralization zone is too deep, and the functional monomers cannot penetrate at that depth [30]. While the data indicates that in 6th-generation adhesives, the bond strength is well to dentin (20 MPa), the bond strength to enamel is at least 25% weak compared to 4th and 5th-generation adhesives [9]. Seventh-generation adhesives were introduced almost two decades ago. They are self-etching systems in one bottle. All adhesive components are incorporated in one bottle "all in one" [30, 34]. The adhesive protocol is greatly simplified. However, from a chemical point of view, it is a challenge for good adhesion to incorporate all components in one bottle. Here the bond strength can reach 25 MPa [30]. Furthermore, they are generally more hydrophilic than two-step self-etching systems once placed and polymerized. This condition makes them more prone to water sorption, limits the depth of resin infiltration into the tooth and creates some voids in the adhesive layer [35]. The clinical and scientific data on these adhesives proves they are hydrophilic and degrade more rapidly than 6th-generation adhesives [36]. The self-etching systems are divided into three groups according to the concentration of acid monomers and pKa (constant of acid dissociation –it represents the acid power of these monomers): aggressive action (aggressive), moderate action (moderate) and soft. Aggressive systems completely dissolve the smear layer. They perform a zone of hybridization like the fourth and fifth-generation systems, whereas the soft self-etching systems generate a fragile hybridization zone [34]. At the end of the first decade of the 21st century, the first adhesives from eight generations contain nanosized fillers. In the new agent, the addition of nano-fillers with an average particle size of 12 nm increases the penetration of resin monomers and the hybrid layer thickness, improving the bonding system's mechanical properties [37, 38]. It improves the bond strength of the enamel and dentin [39]. Based on the manufacture, nano-particles acting as cross-links will reduce the dimensional changes [37, 38]. It is important to note that the types of nano-fillers and the method by which these particles are incorporated affect the adhesive viscosity and penetration ability of the resin monomers into collagen fiber spaces [38]. Nano-fillers, with dimensions larger than 15-20 nm or content of more than 1.0 percent by weight, can increase the adhesives' viscosity and may cause accumulation of the fillers in clusters. The clusters can act as flaws which may induce cracks and cause a decrease in the bond strength [38]. Although Nakabayashi [19, 20] considers that micromechanical bonds are most important for adhesion, forming a zone of hybridization, the chemical interaction provides good hermetical sealing and does not permit microleakage. Microleakage is a serious problem at the adhesive obturations [40, 41,42, 43]. Acid monomers, which are included in the composition of adhesive systems with total-etch and self-etching systems like PENTA, 4-MET, 10-MDP, and phenyl-P, form a strong ionic bond with Ca^{2+} cations from hydroxyapatite crystals, formed stable salt, hardly insoluble in water [44, 45, 46]. It is paying attention to the functional monomer 10-MDP because it forms an ionic bond with the Ca^{2+} cations and a covalent bond with phosphate ions from apatite crystals [45]. When this monomer is added to the self-etching systems' composition, it significantly improves bond strength [47, 48]. Other authors reached a similar conclusion according to 10-MDP and 4-META when they are included in the composition of self-etching adhesives [49]. Investigators stated a high bond strength at the cementation of fiber posts with luting self-adhesive resin cement containing 10-MDP [50]. 4-META and 10-MDP, except for chemical adhesion to hydroxyapatite crystals, it is found that they stable interact with the collagen matrix of the dentin, as 10-MDP ensures more stable interacting because of the more hydrophobic character of its molecule [51, 52].

Conclusion

Therefore, it is assumed that the micromechanical bond has a major role in adhesion, and the chemical interaction of the functional monomers with the hard dental tissues, especially the dentin tissues, contributes to the more intimate and durable connection between resin composites and hard dental tissues.

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