Review Article

Modern Adhesive Strategies: A Review of Literature

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Abstract

It is known that clinical success or failure of composite restorations rely to great extent on the quality and performance of the bonding system used juncture of teeth and restoration. Considering the current review, this paper focuses on enhancing knowledge regarding the concept of adhesion as well as ways of resin-dentin bond deterioration, while also enlisting the recent existing projections to overcome the challenges of dentin bonding.

Keywords: Strategies; Adhesive; Phosphoric; Acid

Introduction

Adhesive strategies have advanced rapidly in the past years. The major problem with dental adhesives is to provide a similarly active bond to the enamel as well as dentin. Dentin bonding continues to be more challenging than bonding to enamel, and therefore often requires multiple steps [1]. Hence, currently used adhesives are considered technique sensitive.

Therefore, different adhesive strategies have been tried to obtain an adequate bond to dentin as well as enamel and also to prevent this bond from degrading with time.

Etch and rinse adhesives

Focuses on increasing the perviousness of resins to enamel as well as dentin. Acid-etching of dentin of around 30-40 wt% phosphoric acid results in complete demineralization of the superficial of the intertubular dentin matrix and results in the formation of nanometer-sized porosities in the primary collagen fibrillar region [2]. The concept of "wet-bonding" advocates keeping the dentin moist prior to bonding. Water is believed to retain the unprotected collagen network's flexibility as well as permeability, and hence suitable for monomer infiltration [3,4]. Drying etched dentin surface by use of air can result in not only shrinkage but also the degradation of the flimsy collagen system which hinders moistening as well as infiltration of the conditioned surface by the monomer [5,6]. However, in case the water within the collagen system is incompletely displaced, resin polymerization within the hybrid layer is likely to be affected. This phenomenon is known as "overwetting" [7]. Excess water causes separation of the monomer components phases causing weak bonds as well as partially closed tubules. This is among the significant hindrances of etch-and-rinse adhesives [2]. The advantages of etch and rinse adhesives include- a high bond strength, as well as the ability to bond to mineralized tissue as well as metal, amalgam, composite and porcelain. However, due to the multiple steps involved, it is technique sensitive.

Self-etch adhesives

These types of adhesives possess acidic monomers that concurrently 'condition' as well as 'prime' the tooth structure. Hence, they are perceived to be friendly to users and also, not so sensitive to technique [8,9]. A significant advantage of self-etch adhesives is their reduced occurrence of operative sensitivity as a result of their less aggressive nature and more shallow communication with dentin, which makes the tubules greatly clogged smear plugs [10].

The advantages of self-etch adhesives include- reduction in the number of steps as no separate etching or post- etch rinsing is required, and also a reduced post-operative sensitivity.

Major shortcomings of self-etch adhesives

They are intricate combinations of hydrophilic as well as hydrophobic mechanisms, and are thus, considered as 'compromise' materials. Reduced instantaneous bond strength is seen when related to that obtained with multiple-phase adhesives [11]. Studies indicate amplified interfacial nano-leakage [12]. Single-step adhesives with high levels of HEMA, imply increased water sorption [13]. While phase-separation is seen when HEMA-free adhesives are used [14]. Also, mixing all ingredients into one bottle results in a reduced shelf-life [15].

Ethanol wet bonding

Here, focus is on the idea of how water from interfibrillar as well as intrafibrillar compartments can be replaced with the help of ethanol to generate a relatively hydrophobic, demineralized collagen matrix to be used by hydrophobic resin monomers during the infiltration process [16-18].

The majority of the "hydrophilicity" of acid-etched dentin substeate is a result of the availability of water [19]. Adhesive monomers are required to dislocate water from the collagen in case they are required to create very close contact with collagen fibrils. Nonetheless, since dental monomers' molecular masses range between 100-580g/mol, their molarities (0.3-5 mol/L) are just a segment of the molarity of water (55.6 mol/L). Therefore, hydrophilic monomers like hydroxyethyl methacrylate (HEMA) have no ability to displace a reasonable amount of water from collagen fibrils. This can be evaded in case ethanol (17.1 mol/L) is used in place of water in acid-etched dentin. This implies that filling the interfibrillar spaces using ethanol is more likely to make the dental matrix more hydrophobic [17].

In a study evaluating the effect of wet bonding using either water or ethanol on the degradation rates of hybrid layers for 18-months, the results for the bond strength as well as transmission electron microscopy (TEM) showed that the adoption of the ethanol wet-attachment mechanism is feasible for enhancing the resin-dentin bond resilience [20].

It is known that pulpal pressure has a negative impact on dentin bonding. This deterioration of bond strength increases with the increase in the depth of the cavity in the dentin. However, it has been seen that where continuous ethanol replacement procedure with virtual pulpal pressure is used in about 4 minutes to accurately conduct ethanol wet-bonding, water detaches from the collagen intrafibrillar spaces, causing a higher intramolecular hydrogen bonding between collagen molecules which in turn shrinks the fibrils [21].

Hydrophilic photoinitiator system

Every current dental adhesive has specific hydrophilic methacrylates as well as hydrophobic dimethacrylates to necessitate their bonding process with dentin and also, to restorative materials appropriately [22].

Nano-phase separation is mostly visible in simplified adhesives due to the concurrent occurrence of hydrophilic as well as hydrophobic mechanisms [23]. Ye., *et al*. with the help of atomic strength microscopy imaging established that there exists a nano-scale phase dissociation for every inter-connected polymethacrylates associated with BisGMA/HEMA as well as water absorption [24].

As camphorquinone (CQ), which is a known photo-initiator, is hydrophobic, it is arguable that hydrophilic monomers might undergo suboptimal polymerization as a result of unsuitable polymerization instigation. To enhance the extent of conversion, adoption of additional hydrophilic photoinitiators, like diphenylphosphine oxide (TPO), phenylpropanedione (PPD), and bisacylphosphine oxide with the help of standard CQ initiation is suggested [22].

Research linking investigational adhesives possessing TPO-related photo-initiators alongside their viable equals possessing CQ recorded similar DC values [25]. A different study, the TPO registered an efficiency higher than CQ, phenylpropanedione (PPD), as well as bisacylphosphine oxide after the polymerization of a meth-

yl methacrylate monomer comprising of a unit with light halogen [26]. A parallel research indicated that there was an increase in extent of conversion of resin combinations when TPO was used alone using ethanol and water each 10%. That is, where TPO was mixed with CQ, the extent of conversion values generated were similar to when CQ was used alone [22].

Molecular interaction and chemical bonding

Each self-etch adhesive possesses a certain efficient monomer that governs its true adhesive conduct [27].

The chemical reaction is attained with the help of precise efficient monomers like 10-methacryloyloxydecyl dihydrogen phosphate as well as 2-methacryloxyethyl phenyl hydrogen phosphate [2]. Additionally, evidence by X-ray photoelectron spectroscopy indicates that any chemical attachment prompted by 10-MDP is extremely real and steady in water compared to that provided by 4-MET and Phenyl-P [27]. The rate at which these monomers' calcium salts dissolve as determined by the atomic absorption spectroscopy (AAS), is contrariwise associated with their possible chemical bonding [27].

It has also been observed that the strength of bonding to dentin of the 10-MDP-related double phase self-etch adhesive Clearfil Mega Bond retained their high rates after long-term thermo-cycling. On the other hand, the power of the UniFil Bond, possessing 4-MET, relatively reduced after 100,000 cycles, while the strength of Clearfil Liner Bond II possessing Phenyl-P, progressively reduced after exposure to thermo-cycling for quite some time [28].

The functional group of Phenyl-P ionically bonds to Ca at the HAp superficially. During stage 2, Phenyl-P-Ca bonds effortlessly separate in the mixture. As such, Phenyl-P greatly decalcifies apatite if exposed to collagen strands. Additionally, the TEM of adhesive-dentin interface generated by the Phenyl-P-related adhesive indicated that nearly every apatite was broken down and also, collagen unprotected at about 1 μm deep [2].

Comparing 4-MET and 10-MDP, the former has a weak chemical bonding ability [41]. Such frail sensitivity to apatite of 4-MET results in the development of a submicron fusion coating made of apatite minerals that stick to collagen strands. Also, the TEM of adhesive-dentin junctions generated by the 4-MET-related adhesive revealed comparatively light reaction with dentin [28].

Unlike Phenyl-P and 4-MET, the hydrogen phosphate part of 10-MDP produces ionic attachments to Ca at the apatite surface during the initial stages. Such bonds rarely separate in their second stage. X-ray diffraction (XRD) confirmed that 10-MDP uninterruptedly establishes a frequently coated form around the apatite structure.

Adhesion-decalcification concept

The pKa rate or dissociation constant of every acid is perceived to be a chief constraint that regulates the way particles react with the rest of the mineralized tissues [29]. The amount of decalcification of hydroxyapatite or dentin is higher when acids with a high pKa rate are used, and vice versa. Consequently, there is no precise explanation of mechanisms regarding why specific molecules effectively interact with tooth tissues unlike others but instead brutally decalcify it [30]. How molecules react with tissues containing HAp is discussed 'Adhesion-Decalcification or A-D concept' [30].

It implies that in the beginning, every acid chemically bonds to the calcium of HAp (during the initial phase). This happens after phosphate as well as hydroxyl (OH⁻) ions are generated by HAp into its own mixture while the surface retains its electro-neutral state.

Whether molecules retain their bonds (during the second stage, first option) or separate (PHASE 2, OPTION 2), relies on how suitable specific calcium salts are. Molecules such as 10-MDP and also polyalkenoic acids have a very high likelihood of bonding chemically to Ca of HAp (PHASE 2, OPTION 1). This chemical bond forms stable calcium-phosphate as well as calcium-carboxylate salts correspondingly, with just an incomplete superficial-decalcification impact. Nonetheless, molecules such as phosphoric as well as maleic acid, and active monomers from the self-etch adhesives such as 2-(methacryloyloxyethyl) phenyl hydrogenphosphate as well as HEMA-phosphates greatly separate (During PHASE 2, OPTION 2). Phosphate ions that are negatively charged will displace the positively charged Ca ions to a specific depth dependent on the time of application. This forms a great decalcification or 'etching' effect, which in turn results in a comparatively deep (3–5μm) hybrid coat at dentin without any HAp crystals [1].

Nevertheless, the model is restricted to explaining 1 mono-, 2 di-, 1 tri-, as well as 2 poly-carboxylic acids reacting with synthetic HAp that contains a specific mineral rather than hard tissues from humans which known to possess apatite structures with varying crystallinities [31].

Nano-Layering

The self-assembly of nano-layered components, similar to the progression of 'biomineralization', is considered to offer greatly

advantageous purposes [32]. In the field of engineering, nano-layering is seen as a way of enhancing the general presentation of materials, as well as their resistance against impairment or aging more precisely [33].

Lately, self-assembled nano-layering is said to result from reactions of active monomer 10-MDP, primarily reacting with synthetic hydroxyapatite [34] and with enamel and dentin later [35]. It has been argued that this kind of nano-layering around the MDP/Hap junction might enhance bond durability [36]. The nano-layered components are characterized by their strong hydrophobic nature may be used to shield the hybrid coat against degradation making the remaining HAp more resilient to acidic dissolution [37,38].

In a study, MDP-Ca salinities were generated by two viable adhesives that possess MDP, a progression that presented as interfacial nano-layering. Other studies have concluded that the nano-coating strength, and the XRD-edge strength on behalf of nano-coating, was directly comparative to MDP concentration. The method of nano-layering is described as, at the time of scrubbing MDP-possessing adhesive onto dentin, and some minerals are partly removed from the layer to reach the submicron. Upon incomplete disbanding of HAp, Ca ions are generated and released and diffused in the hybrid coat collecting MDP particles into the nano layers. This whole procedure is steered by formation of MDP-Ca salt. Theoretically, one MDP particle is about 1.95 nm in size. Therefore, dual MDP particles are about 3.90 nm in size. These measurements give an approximation of nano-layer of MDP at artificial Hap to be around 4-nm-in thickness. Every layer of this "nano-coating comprises of dual 10-MDP particles together with their methacrylate part focused towards each other as well as their active hydrogen phosphate part that are focused in each other's opposite direction [38].

Nano-layering has been seen to improve dentin bond strength, results in a longer shelf life and durable marginal seal. However, biological consequences including oxidative stresses, inflammation and impaired clearance of these materials need to be addressed. Studies regarding the long term toxicity of these materials are not available.

Creating acid-base resistant zone (ABRZ) at enamel/ dentin-adhesive interface

The advancement of recurrent caries is more likely to be retarded by the increasing strength of tooth-resin interface against acid [39]. Observation made by SEM at dentin-adhesive junctions indicated availability of an acid-base resilient region under the hybrid layer in self-etch adhesive structures following the acid-base attacks [40]. Most studies have held that the sound structure of dentin ABRZ is extremely adhesive-material reliant and also, that ABRZ is developed within self-etch adhesive structures rather than in etch-and-rinse adhesive structures [41]. Based on TEM proof, the ABRZ possess heavily organized apatite crystallites with characteristics that are totally different from the hybrid layer [42].

It is evident that the formative mechanism is not clear. However, it is presumed that the diffusion of any monomers past the hybrid layer into the tooth material as well as the organic reaction amid the efficient monomer and hydroxyapatite is likely to result in the development of ABRZ. It is suggested to refrain from removing detin minerals using phosphoric acid, since the approach consists of ample penetration of monomers and also minimizes the opportunity of any active chemical bonding as well as shielding of apatite against acid-attack [43].

Therefore, it is proposed that the ABRZ design gotten from every adhesive structure may be seen as an indicator to foretell its bonding longevity to tooth substrates [44].

Calcium- chelation dry bonding

For most clinicians, wet conditions required for phosphoric acid-etched dentin bonding continues to be confusing.

Water has for long been perceived as a major critical barrier for etch-and-rinse adhesives to effectively bond to dentin. However, the modulus of elasticity of entirely demineralizede dentin is significantly low at around 134 kPa, such that nearly all pressure is likely to result in its breakdown. In case such surfaces are air-dried to drain superficial water, collagen strands that are demineralized definitely collapse to establish a coat of impervious collagen [45].

Where one is able so to selectively demineralize mineralized dentin to specifically get rid of the interfibrillar apatite crystallites whilst maintaining the collagen fibrils stiffness consisting intrafibrillar minerals, there is no need of suspending the strands that are incompletely demineralized in water to retain the bond. This therefore helps address the breach amid wet and dry-bonding by ensuring that resin monomers are infiltrated by dry air, mineral-depleted dentin.

As is well known, collagen fibrils show size-exclusion characteristics. How these collogen molecules are organized in their respective fibrils forms a molecular-sieve effect except for molecules

that are not greater than 6 kDa [46]. However, those between 6-40 kDa in size can incompletely reach the intrafibrillar water spaces of any collagen strands that are demineralized. These water spaces are partially unreachable by particles whose sizes are greater than 40 kDa [47]. Given that phosphoric acid displaces calcium from dentin with the help of hydronium ion (19 Da), the accessibility of hydronium ions water spaces in collagen fibrils in order to soften intrafibrillar apatite is unrestricted. However, ethylenediaminetetraacetic acid (EDTA), chelating agent (292 Da), is suggested to be used in place of phosphoric acid to etch enamel as well as dentin. The chelating agent is small in size which prevents it from completely getting rid of extrafibrillar minerals from dentin. Practically, it is obvious that one may opt for larger polymeric acids or use chelators more than 40 kDa in size so as not demineralize intrafibrillar minerals from dentin matrix but rather use selective demineralization [47].

Researchers have proposed two ways to achieve distinctive extrafibrillar demineralization of dentin, that also prevent the collapse of dentin in case they are air-dried. First, a PAAN polymeric chelator can be used with MW more than 40 kDa. This approach takes time and may also not be practically clinical therefore, extrafibrillar minerals can be entirely eliminated and the adhesive resin monomers can easily diffuse through available wide interfibrillar channels. Second, protocol is quicker, and includes a 30-second application time. This was used by Bouncier for his research on enamel bonding [47].

More research is needed to assess the exclusion of size as one of the characteristics of frequently adopted adhesive resin monomers of various molecular sizes in incompletely as well as entirely demineralized extrafibrillar paths of incompletely demineralized dentin powder. Studies may also combine the above suggested extrafibrillar demineralization approaches through conditioning of dentin with the help of a polymeric chelating agent greater than the size of 40 kDa in size for 60s rather than 30s. This will help utilize the benefits of the two protocols. As such, PAAN is not just the only option: the available plethora of polymeric calcium chelators can be used to achieve this objective provided they are biocompatible for intraoral custom [48].

Currently Unite (3M Unitek), Smartbond (Gestenco) and Transbond MIP (3M Unitek) are some of the moisture active bonding systems available. However, their long-term bond strengths to enamel as well as dentin have been found to be inferior to the conventional bonding agents.

Conclusion

Although "reality falls short of a conceptualization", dental researchers have brought long-debated issues of presenting adhesives with the ability to effectively bond to dentin as well as enamel instantaneously to fruition. However, none of the ideas presented is perfect. Therefore, a lot of work and research needs to be done to improve different bonding structures.

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