Adhesion - New Approaches

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Abstract: ***Adhesive dentistry is the one entity in dentistry towards which considerable studies has been done in recent years. The drawback with Contemporary dental adhesives is the disintegration of resin-dentin bond with time. Today growing efforts are made to simplify and shorten the bonding procedures so as to improve the longevity of resin restorations. Numerous simplified adhesives have been introduced to dentistry within the last few years. Despite significant improvements in adhesive systems, the bonded interface of dental hard tissues with resinous restoratives remains the weakest area of tooth-coloured restorations. In this review, the modifying methods of adhesive materials to improve the longevity of resinous restorations are summarized***.

Keywords: super dentin, smart materials,10-MDP, MDPB

1. Introduction

One of the greatest challenges in restorative dentistry is to obtain an effective bond of the tooth-restoration interface. Several obstacles must be overcome to accomplish effective bonding and to achieve durable restorations that seal the margins and provide some form of resistance to recurrent caries lesions.

Composite restorations depend on adhesive systems which form a micromechanical bond with the tooth structure. The original multicomponent bonding systems of composite restorations are gradually being replaced with simplified, consolidated adhesive systems that are more user-friendly.

Most of the current dental adhesives reveal excellent immediate and short-term bonding effectiveness, but the durability and stability of resin-bonded interfaces still remains questionable. Therefore, it is necessary to refine the adhesive materials for breaking this issue [1]. Numerous studies have been designed in pursuit of more stable resin-dentin bond. In this review, the modifying methods of adhesive materials to improve the longevity of resinous restorations are summarized.

2. Tooth - as a bonding substrate

Unlike enamel bonding which can be obtained relatively easy, bonding to dentin has continued to be a challenge. This is partly due to the biological characteristics of dentin, like high organic content, tubular structure with presence of odontoblastic processes, continuous moist condition due to presence of dentinal fluid, intratubular pressure and permeability of the dentin. This humid and organic nature of dentin makes bonding to this hard tissue extremely difficult.

When tooth structure is cut with a bur or other instrument, the residual components form a ‘‘smear layer’’ of debris on the surface [2]. This debris forms a uniform coating on enamel and dentin and plugs the entrance of the dentinal tubules, reducing the permeability of dentin.. Smear layer must be dissolved or made permeable so the monomers in the adhesives can contact the dentin surface directly.

3. Recent Trends in Dentin Bonding

- **Acid – base resistant zone (ABRZ)**

Monomer penetration into dentin and its polymerization in situ creates a hybrid layer, which is essential for obtaining good bonding to dentin. Theoretically, the hybrid layer can provide marginal sealing of the cavity and resist against acid challenge to prevent secondary caries [3]. However, it was reported that none of the adhesives currently available could completely eliminate nanoleakage along the dentin-restorative interface. Of all acidic monomers present in the self etch adhesives, 10-MDP shows highest chemical bonding potential. The ability of 10-MDP to readily form an ionic bond with hydroxy apatite crystals results in creating a highly favourable bonding substrate for long term durability [4]. Tsuchiya et al. (2004) reported the presence of an acid base resistant zone below the hybrid layer with self-etching adhesive systems subjected to an artificial secondary caries attack. The thickness of this layer varies from 0.5 – 1 micron meter, which is more pronounced in carious dentin than in normal dentin. This zone along with lower part of the hybrid layer is termed ABRZ and the dentin is known as “super dentin”

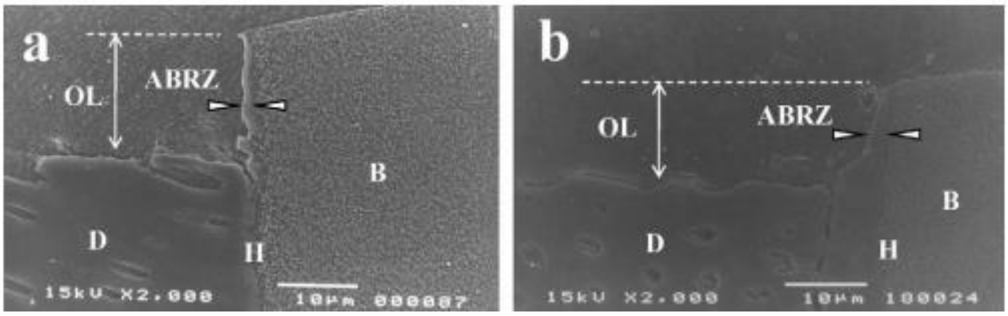

Figure 1: SEM observations at the interface between Clearfil SE Bond and dentin after acid—base challenge (3500) (Inoue et al.). (a) Intact dentin and (b) caries-affected dentin. OL: outer lesion; B: adhesive; H: hybrid layer; ABRZ: acid—base resistant zone; D: dentin. An acid—base resistant zone (ABRZ), approximately 1 mm thick, was observed beneath the hybrid layer (H) for the intact dentin (left), while a thicker acid—base resistant zone, approximately 1.5 mm thick, was created in the caries-affected dentin (right) (Toru Nikaido et al, Japanese dental science review)

- **Adhesion- Decalcification concept**

The recent concept of adhesion with self etch adhesives is based on the PH of the acidic monomers, they either decalcify or bond chemically with hydroxyapatite. This led to adhesion – decalcification concept, as described by Van Meerbeek [5]. According to this concept, there are 2 phases. In phase one, the acidic monomer attacks the dentin surface, resulting in the release of calcium and phosphate ions, the typical acid etching process takes place between the conjugate base present in the acid and the calcium of hydroxyapatite forming calcium salts. Phase two has two options, if the salt formed is stable, then no further interaction takes place (phase 2, option 1). There is minimal etching and partial dissolution of hydroxyapatite. On the other hand, if the calcium salts debond, the acidic reaction continues leading to further etching (phase2,option2), here hydroxyapatite is completely dissolved, exposing the collagen fibrils

- **Inorganic Fillers or Remineralizing agents and Nanotubes**

The loading of adhesive compositions with fillers and nanoparticles has significant reinforcement effect of the adhesive. Carboxylic acid-functionalized titanium dioxide, copper, zinc oxide, silver nanoparticles have been used to reinforce the organic matrix of resin adhesives, and thus improving physico-mechanical properties of the material, and consequently, bond strength between the restoratives and dental substrates [6]. zirconia nanoparticles are also can be incorporated into the primer or adhesive of a commercial three-step etch-and-rinse adhesive system (SBMP, Scotchbond™ Multipurpose™, 3M ESPE), resulting in increased dentin bond strength. The formation of a strong adhesive interface is usually associated with a higher resistance to hydrolytic phenomenon, which may enhance bond durability. Once the hybrid layer is strong, water uptake is reduced, hydrolysis is diminished, and proteases activity is retarded, thereby reducing the rate of bond degradation over time [7].

Currently, studies have reported on biomimetic "smart materials" that possess remineralizing potential. Bioactive silicates, such as calcium/sodium phosphosilicate (Bioglass 45S5), have been combined with hydrophilic, biodegradable polymers in order to allow for lower degrees of collagen degradation [8].These silicate-containing adhesives may show biological activity when exposed to biological fluids, thereby producing ionic dissolution products that will directly act at the hybrid layer level. However, this mechanism is controversial and must be further explored: on one hand, adhesive degradation may release the silicates, thus enhancing bioactivity, but on the other hand, degradation of adhesive components could lead to reduced mechanical properties, which would ultimately compromise bond durability [9]. This field is new in adhesive dentistry and needs further investigation.

In recent years, polymer-nanotube composites have been increasingly studied due to their interesting properties and potential for a wide range of applications. In these materials carbon nanotubes are used as inclusions in various matrices to improve electrical, mechanical, or thermal properties [10]. In particular, due to their high Young's modulus CNTs are considered promising candidates for mechanical reinforcement of polymers. There are, however, a number of issues to be resolved, with the control of polymer nanotube interfacial bonding as the main aim.

- **Collagen cross linkers and Protease inhibitors**

Resin/dentin bond degradation is a complex process involving the hydrolysis of both the resin and the collagen component of hybrid layers. Demineralized dentin contains bound matrix metalloproteinases (MMPs) and cathepsins in their active forms. MMPs are a family of 30 host-derived proteolytic zinc- and calcium-dependent endopeptidases that, together, degrade practically all extracellular matrix components. Thus, they are important to many biological and pathological processes. MMP-1 and -8 (collagenase), -2 and -9 (gelatinase) and -3 (stromelysin) have been found in normal dentin [11]. Under normal circumstances, MMPs are secreted into the ECM as inactive proenzymes which require activation by proteinases, chemicals, or low pH to degrade matrix components. When dentin MMPs are exposed and activated by self-etch or etch- and -rinse adhesives, they degrade type I collagen fibers, as well as influence dentin hybrid layer and bonding strength. With both self-etch or etch- and -rinse adhesives, denuded collagen fibers can be seen at the bottom of the dentin hybrid layer, because of incomplete resin monomer infiltration [12]. Once MMPs are activated, they adversely modify dentin bonding durability.

Chlorhexidine and minocycline have received increased interest as MMP inhibitors as they compete with MMPs for calcium and zinc ions as metal chelating agents to inhibit their activity. Specifically, MMP-2, -8, -9 activity are reduced and this slows collagen degradation in the dentin hybrid layer and improves bonding strength. A 2% CHX solution applied to a demineralized dentin surface and analyzed with enzyme spectrum detection and nanoleakage studies confirmed that CHX could inhibit gelatinase activity and maintain the stability of the bonding interface within few months after restoration. Tetracyclin compounds can also prevent collagen degradation and improve stability in the dentin hybrid layer. Chemical modification of tetracyclin class members such as doxycycline and Minocyclin can also be used as nonspecific MMP inhibitors for treatment of oral diseases. However chlorhexidine is water-soluble and may undergo leaching from the hybrid layer, impairing its long-term anti-MMP effectiveness.

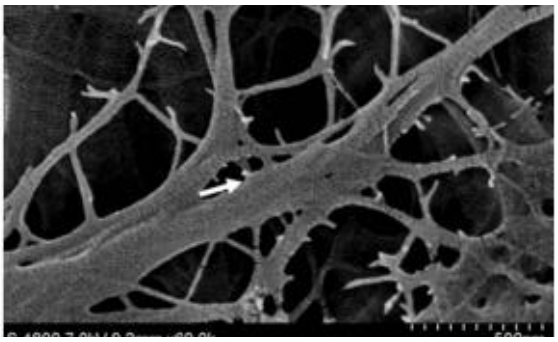

Figure 2: Collagen fibers treated with chlorhexidine, collagen fibers exposed and staggered in a mesh formation (Int J Clin Exp Med ;8(7):10793-10803)

A new alternative to the inhibition of proteases by inhibitors, is the treatment of demineralized dentin with cross-linking agents that can inactivate the catalytic site of these enzymes. The cross-linker 1-(3-dimethylaminopropyl) carbodiimide (EDC) is capable of forming covalent peptide bonds between proteins by activating the free carboxyl group of glutamic and aspartic acids present in protein molecules [13]. This results in the formation of a O-acylisourea intermediate that reacts with the epsilon amino group of lysine or hydroxylysine in an adjacent polypeptide chain to form a stable, covalent amide bond. EDC shows no transdentinal cytotoxicity on odontoblast-like cells and is able to increase the mechanical properties of the collagen matrix

- **Laser treatment prior to bonding**

Over the last few years, several studies have demonstrated that laser irradiation of enamel/dentin prior to bonding may result in bond strength enhancement. The two main laser sources used are the Erbium-doped Yttrium Aluminum Garnet (Er:YAG) and Plasma-based lasers [14] . With regard to the use of Er:YAG lasers, current findings have shown that laser irradiation may cause specific topographic changes in the surface of dental substrates, such as removal of the smear layer, evaporation of water and organic content, and the creation of crater-like areas that may contribute to increasing the surface area, key for successful dental bonding. In another study, dentin is treated with a nonthermal atmospheric pressure plasma (NT-APP) laser prior to bonding, thus improving the immediate resin-dentin bonds and allowing for stable bonds after aging. The authors stated that application of the laser created active species, such as carboxyl and carbonyl groups onto the dentin surface, thereby improving wetting and chemical interaction of the adhesive monomers [15].

- **Universal Adhesive system**

Universal dental adhesives were introduced as versatile multifunctional systems with reduced application steps, compatible with all dental hard tissue treatment modalities, capable of bonding to various restorative materials combined with appropriate surface treatments. All the commercial products tested were based on the 10-MDP adhesive monomer with a bonding capacity with dentin, titanium, metal alloys and polycrystalline ceramic [16]. These novel multi-mode adhesives reduce the complexity of clinical application procedures. Adhesives in this category may be used as etch-and-rinse adhesives, self-etch adhesives, or as self-etch adhesives on dentin and etch-and-rinse adhesives on enamel.

Functional monomers like MDP (10-methacryloyloxydecyl dihydrogen phosphate) are the principal ingredient of recently developed multi-mode adhesives, as they play a major role in chemical adhesion to dentin. The addition of acidic functional monomers to universal adhesives, such as MDP, distinguishes them from the classical 1-step SE adhesives. The molecule MDP has been shown to interact with hydroxyapatite through a dual adhesion mechanism: (1) stable ionic bonding to calcium is formed through a nanolayered structure of MDP-Ca salts at the interface with hydroxyapatite. Such hydrophobic nanolayering is deemed to improve the long term durability of dentin and enamel bonding and (2) greater enamel etching potential for MDP compared to other acidic functional monomer [17].

Calcium is depleted from the dentin surface when dentin is etched with phosphoric acid. Without calcium it is unclear how MDP-containing adhesives are able to bond ionically to etched dentin through nanolayering. Therefore, MDP-containing SE adhesives may need to be applied only on un etched dentin, while ER adhesives are more effective on enamel. The only option is to use the selective enamel etching technique, in which only enamel is etched with phosphoric acid. In fact, etching enamel may not only enable the characteristic micromechanical interlocking into the enamel microporosities, but also potentiates the chemical bonding of MDP around the enamel crystallites in etched enamel resulting in higher bond strengths than other adhesives without MDP

- **Antioxidants**

Clinical procedures like bleaching with hydrogen peroxide or treatment with NaOCl may generate and retain oxidizing species in dental substrates, thereby hampering polymerization of resin-based materials (e.g. adhesives, restoratives). In order to eliminate any oxidizing species from the dental structure, the use of antioxidants has been suggested as an effective strategy. several agents are available for that purpose like proanthocyanidins, noni fruit juice, vitamin C, vitamin E, and quercetin[18]. These agents strengthens the hybrid layer and became available for further reaction with products of degradation, leading to a late polymerization process, and consequently, to improvement of the resin-dentin bonds over time.

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It seems that the use of antioxidants holds importance for increasing bond strength between the adhesively-bonded restorations and substrates that underwent an oxidizing process, with the possibility of preventing their resin-dentin bonds over time [19].

- **Antibacterial Self etch Dental Adhesive system**

The risk of recurrent caries is increased by residual bacteria in tooth restoration interface, which remains a challenge in dentistry. In order to avoid this adverse condition, adhesive systems should present a long-lasting antibacterial activity for bacteria that enter this interface, leading to microleakage. some antimicrobials freely dispersed into adhesive systems such as antibiotics, quaternary ammonium compounds, glutaraldehyde and fluorides have been extensively evaluated. However these freely dispersed agents are inappropriately released from restorative material and result in decreased bond strength for restoration [20].

Other studies assessed the use of quaternary ammonium-based antibacterial monomers into dental resins such as 1,2-methacryloyloxydodecylpyridinium bromide (MDPB). MDPB shows antibacterial activity against Streptococcus mutans, Lactobacillus casei, and Actinomyces naeslundii. This monomer is incorporated into an adhesive system and is now commercially available as Clearfil™ Protect Bond. some studies have reported limitations in their use. Clearfil™ Protect Bond exhibits an antibacterial effect for only seven days [21]. Thus, the MDPB molecules that were not polymerized were leached out of the adhesive system leading to a higher antibacterial effect but only in a reduced time interval. In addition, quaternary ammonium compounds of low molecular weight as MDPB can have cytotoxicity to human pulp cells, which compromises their clinical safety

Another antibacterial nano particle, chitosan is a collective name to describe a family of linear polysaccharides composed of β-1→4 linked D - glucosamine, with some residual interspersed N-acetyl-D-glucosamine.. Chitosan is bio-adhesive, a property which determines an increased retention at the site of application. Chitosan is a very versatile polymer that can be readily modified to endow it with peculiar physical-chemical and/or biological properties [22]. The chemical linkage of methacrylate moieties onto the chitosan chain was recently exploited to prepare rechargeable antimicrobial coatings on polyurethane.

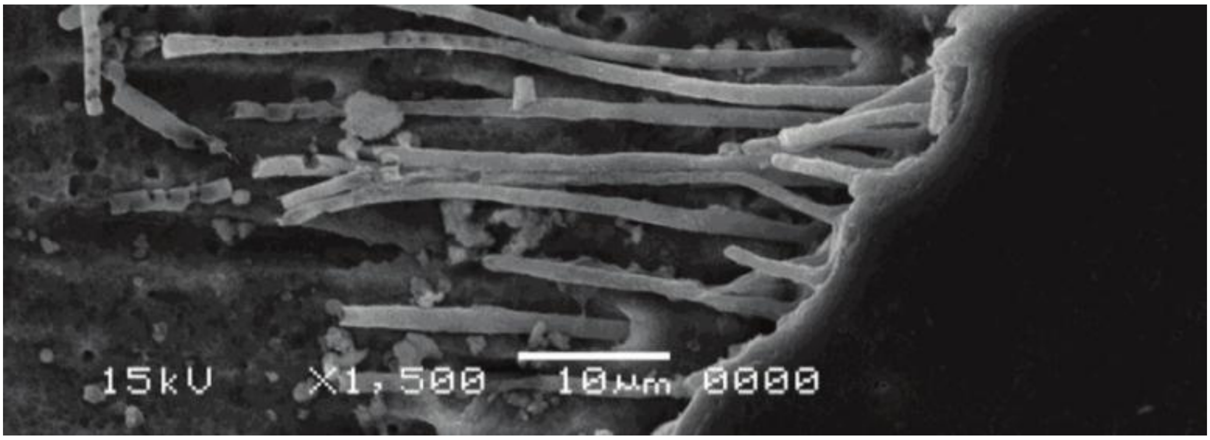

Figure 3: Scanning electron microscope of specimen treated with chitosan nanoparticles 0.2% at 3 months aging period showing long resin tags chitosan particles entrapped within dentin surface.(Int. J. Mol. Sci., 15, 8998-9015)

Novel antimicrobial agents are needed and much work has been devoted to developing highly efficient compounds that are also less susceptible to development of resistance by bacteria. Quaternary ammonium methacrylate polymer (QAMP), a poly (dimethylaminoethyl methacrylate-co-octyldimethyl ammonium ethyl methacrylate bromide-co-methyl methacrylate-co-butyl methacrylate was then incorporated into a self-etching adhesive system. The self-etching adhesive containing QAMP had antibacterial activity against S. mutans and was particularly recommended for reducing recurrent caries [23]. Due to its high molecular weight, QAMP demonstrated a lower migration from the adhesive system compared to MDPB. In addition, QAMP is a non-volatile and chemically stable polymer that is not permeable through the oral mucosa in contrast to the main problems of the chemically-related quaternized monomers. However, further studies are required to evaluate the behavior of QAMP in adhesive systems concerning their physicochemical properties, e.g., resin–dentin bond strength (μTBS) and degree of conversion (DC) which are strongly related to dental restoration longevity [24].

4. Conclusion

Improved adhesive materials have made composite restorations more reliable and long standing, and it is important to examine advances in the practice of adhesive dentistry with the latest methods. In future with thecontinued development of new technology, it will be the dentist who makes decision to make the right choice

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