Effect of surface treatment on adhesion to dentin

Ferry Jaya¹, Yosi Kusuma Eriwati²
¹ Graduate Programs of Dental Materials
² Department of Dental Materials
Faculty of Dentistry, Universitas Indonesia

ABSTRACT

Background: Lack of adhesion in composite resin restorations can be detrimental to the bond strength between dentin and bonding agents. The selection of bonding systems with its surface treatment to dentin are crucial in this case. Bonding to dentin is more difficult than enamel since dentin contains more organic matrix and liquid of dentin tubuli. To overcome this condition, dentists should undertake good adhesion to dentin by choosing the right bonding systems. Purpose: To discuss the development of surface treatment and its effect in adhesive system to dentin and also gives clinicians a new perceptive of adhesive system so that clinician can decide which adhesive’s material will be chosen to have a long lasting composite resin restoration.

Reviews: With new development of bonding systems, the seventh-generation bonding systems are the “all-in-one” adhesives that combine etch, prime, and bond in a single solution, and recently, a new material which combine adhesive system with resin technology has been introduced as a self-adhering flowable composite that eliminates the need for a separate bonding application step for direct restorative procedures. Conclusion: Dentists are expected to know this new development to improve their ability to better choose the right bonding system for their patient cases.

Key words: Surface treatment, adhesion, bonding system, dentin

INTRODUCTION

Adhesive dentistry has brought into perceptive the possibility of a more conservative approach to tooth restoration, based on minimal invasive cavity preparation and bonding of resin composite to tooth structure. Therefore composite resin requires an adhesive material called bonding agent to bond to tooth structure.

Dentists often complained on the failure of composite resin, such as fall out restoration or discoloration in its marginal fillings. The gingival wall of cervical cavities were often contaminated and wetted which can lead to microleakage and sensitivity in those area. The development of adhesive system or bonding agent began since 1955 when Buonocore used phosphoric acid as a surface treatment to improve the bond strength. Phosphoric acid etchant as surface treatment can alter tooth structure surface as well as improving the bond strength between adhesive and tooth structure, for example by applying etching, priming and adhesive to enamel and dentin, so called the Total-Etch Tehnique. Total-etch technique can demineralize enamel as well as dentin and can open dentinal tubuli to improve bond strength by creating impregnated resin tags. It has been reported that this total-etch system can cause marginal discoloration and post operative sensitivity. Hashimoto has demonstrated...
that gradual debonding from dentinal surface can occur over a period of time and its adhesive force can decrease by nearly 75% of aging over a 3 year period.

The development of dental adhesives focus on how to simplify its procedure by reducing the application step in order to decrease manipulation time and sensitivity resulting a higher effectiveness of adhesion. The new adhesive development was called Self-etch adhesive system or One step self-etch adhesive that requires only one application step to bond composite (1-SEAs). Surface treatment in self-etch adhesive system usually keep the smear layer as substrate where as the total-etch system will remove all the smear layer. Which is the most effective system between Total-etch and Self-etch adhesive bonding is still in debate and research.

Recently, a new innovation adhesive system was also introduced which combine resin technology of composite and adhesive into one product called Self Adhering Flowable Composite. Self adhering flowable-composite eliminates the need of separate bonding application step with composites for direct restorative procedure. This paper aims to discuss the development of surface treatment and its effect in adhesive system to dentin and also gives clinicians a new perceptive of adhesive system so that clinician can decide which adhesive's material will be chosen to have a long lasting composite resin restoration.

PRINCIPLES ON ADHESION

Adhesion is defined as the attachment of one substance to another whenever they come into close contact with each other. To get a better contact between the two materials, an intermediate layer called an adhesive has to be placed. There are two main theories to observed the phenomena of adhesion, which are: mechanical theory, the solidified adhesive will interlock micromechanically with the roughness and irregularities of the adherend's surface; and adsorption theory, this theory includes all kind of chemical bonds between the adhesive and the adherend, including primary and secondary valences forces. Primary forces are ionic and secondary forces are hydrogen, dipole interaction and Van der Waals forces.

In the formation of an optimally bonded interface, it is required that: the substrate surface is clean; the adhesive can wet the substrate well, so it has low contact angle and can spread onto all of the surface; adaptation to the substrate can produce intimate approximation of the material without entrapped air or other intervening material; the interface can include the sufficient physical, chemical and mechanical strength to resist intraoral forces of debonding; the adhesive can be well cure under the conditions recommended for use.

Adhesion process in dentin is more complex than on enamel because of the composition and structure differences. According to Buonocore 1955, enamel contains less protein and does not collapse when dried which can increase the bond strength of resin to enamel. In contrary, dentin consists of dentin tubuli liquid and has sensitive collagen network. Inaccurate surface treatment on dentin such as over-etch to dentin surface often cause post operative sensitivity.

DENTIN SURFACE TREATMENT

Cleansing of substrate surface oftentimes becomes a technical problem upon applying adhesive into the mouth which is pellicle and smear layer. Pellicle exists in saliva, and smear layer will appear when we prepare tooth cavities. Clinical, Smear layer generally covers the dentin surface after preparing a filling cavity. The porous smear layer of about 1-7 µm is composed of hydroxyl-apatite and altered collagen. Pellicle and smear layer must be removed before bonding to increase surface energy so adhesive can have a good wetting to substrat. High surface energy is needed for the substrate to more likely adsorb adhesive material from the surrounding, and to make an intimate contact.

The smear layer conducted as a barrier that protects the pulp from dangerous stimulus and reduces the flow out of tubuli dentin's liquid. Smear layer can also be used as the substrate which means that the adhesive makes use of the porosities within the smear layer for being partly dissolved or it can be totally removed. However, the most important fact regarding the smear layer and adhesion is that smear layer will prevents any materials from direct contact to solid dentin that can decrease the bond strength of the adhesive to dentin. The smear layer is thought to prevent penetration of monomers into the dentin substrate. Thus, to improve bonding, the smear layer is removed and the underlying dentin surface subsequently demineralized. Therefore to get into close contact to the solid dentin, the smear layer has to be at least partly dissolved and incorporated into adhesive layer or it has to be remove totally.
Perfect adhesion to tooth structure is the primary objective. However, several contributing factors, such as: material physical characteristics, polymerization source, cavity location and configuration, composition of dentin, occlusion components, lack of strict adherence to manufacture’s instructions and inconsistent clinical techniques by the practitioner can diminish restorative success. Dentin surface treatment such as acid etch, air abrasion with aluminium oxide, irrigation with sodium hypochlorite and mechanical cleaning with slurry of pumice can altered the surface energy and dentin permeability, which increases the adhesive penetration into the demineralized collagen matrix and improves the sealing of exposed dentin tubules.

Acid etchant

Acid etching removes the smear layer and hydroxyapatite and modifies the dentin microstructure morphology creating micromechanical retention. Various acid etchant have been used such as: a weak organic acid (e.g., maleic acid), a stronger inorganic acid (e.g., 36-38% phosphoric acid or nitric acid), or a chelating agent (e.g., EDTA).

The main action of etchant is that it heavily alters or removes the smear layer, demineralizes peritubular and intertubular surface dentin and increase dentin permeability by 4 to 9 times. Etchant also exposed collagen fibrils demineralized up to depth 7.5 microns, depth of demineralization depends on: type of acid, its concentration and etching time. Traditional dentin bonding usually requires a previous phosphoric acid treatment, dentin etching with phosphoric acid meaningfully improves the wettability (about 35%), and the dentin surface energy is increased from 42.2-45.7 mJ/m² before phosphoric etching to 46.6 mJ/m² after phosphoric etching.

Surface pre treatment

Newman et al, Galloway and Pashley, Gwinnett found that when using air-powder polisher it would removed superficial smear layer, exposing the underlying substrate and leaving the tubules plugged with cutting debris in dentin so the monomer could penetrate into the dentin substrate more easily. Surface pre treatment with aluminium oxide (25 µm and 50 µm) air abrasion using low air pressure (60 psi) will result an irregular and retentive dentin surface.

Figure 1. SEM images of dentin treated with: (A) diamond rotary instrument (presence of smear layer); (B) 35% phosphoric acid; (C) pumice slurry; (D) pumice slurry followed by 35% phosphoric acid etching (presence of contaminants); (E) 25µm-aluminum oxide air abrasion; (F) 25µm-aluminum oxide air abrasion followed by 35% phosphoric acid etching; (G) 50µm-aluminum oxide air abrasion; (H) 50µm-aluminum oxide air abrasion followed by 35% phosphoric acid etching; (I) sodium bicarbonate air abrasion; (J) sodium bicarbonate air abrasion followed by 35% phosphoric acid etching.
produced small modification of dentin morphology, which was not significantly different from the non-treated dentin. The presence of contaminants from pre-treatments before acid etching may compromise bonding stability. The difference of dentin surface treatment in SEM images can be seen in figure 1. However, the etching effects of the bonding system had a greater influence on the surface changes than the air-powder polishin.

Clinical longevity of the hybrid layer seems to involve both physical and chemical factors such as the occlusal chewing force, and stresses due to temperature changes within the oral cavity that can affect the interface stability. Acidic chemical agents in dentinal fluid, saliva, food and beverages and bacterial products further challenge the tooth/biomaterial interface resulting degradation of unprotected collagen and resin components. As hybrid layer is created by mixture of dentin organic matrix, residual hydroxyl-apatite crystallites, resin monomers and solvents, aging may affect each of the individual components or may be due to synergistic combinations of degradation phenomena occurring within the hybrid layer.

**Adhesion-promoting agents for dentin surface treatment**

When clinicians work on dentin, they have to deal with three problems regarding adhesion to dentin, such as the hydrophilicity, the low surface energy and the sensitive scaffold of collagen fibers in dentin. The hydrophilicity and the solvent composition of the adhesive materials also influence the surface treatment on dentin and the adhesion to restorative materials.

**Hydrophilicity**

Water is an essential component of dentin matrix to prevent the collapse of collagen network after acid etching. However, excessive moisture can adversely affect hybrid layer durability due to degradation of either collagen fibrils or resin materials. To overcome these conditions, an adhesion promoting agent must be used.

The function of adhesion promoting agent such as a hydrophilic primer is to change the surface properties of dentin to promote diffusion of the adhesive into the collagen network and into the opened tubules. The priming process is expected to produce efficient wetting of the exposed collagen fibrils, which displaces any residual surface moisture, transforms a hydrophilic into hydrophobic surface condition, and sufficiently carries monomer into the interfibrillar channels of demineralized dentin.

Adhesive system requires hydrophilic monomers and anhydrous solvents in their formulation to produce high bond strength to moist dentin surface. Example of the hydrophilic monomers are HEMA (hydroxyethyl methacrylate), NMSA (N-methacryloyl-5-aminosalicylic acid), NPG (N-phenylglycine), PMDM (pyromellitic diethylmethacrylate) and 4-META (4-methacryloxyethyl trimellitate anhydride). HEMA was usually used as hydrophilic monomer in adhesive materials. HEMA is a water soluble priming monomer that one could obtain a self-etching, and self priming adhesive with a pH low enough (pH 1-2). HEMA can react either as an acid or a base and displaces water in dentin but is also miscible with most of the monomers of the adhesives. Despite that HEMA also can raise the hydrophilicity of the adhesive, which may in turn increase the risk of water uptake into matrix and decrease the polymerization rate.

**Solvents**

Solvent is necessary to carry out excess water and to provide a proper infiltration of the resin monomers into demineralized collagen matrix. Benefit of solvents are generally improving substrate wetting, aiding to impede the collagen fibrils collapse or to stiffen them. However, solvents must be eliminated after having completed their function because the residual solvent can lead deterioration of adhesive interface by interfering with resin polymerization and decreasing mechanical properties.

Contemporary dentin bonding system presents resinous monomers in combination with solvent such as acetone, ethanol, water or a combination of them. Evaporation capacity of solvent is dependent on the vapor pressure, molar weight and solubility, which means higher the molar weight and vapor pressure contributes to lower evaporation speed. The addition of water to the formulation of ethanol-base adhesive could lead to less technique sensitive dentin bonding because demineralized dentin surface could be dried without compromising bond strength values. Solvent evaporation after application to dentin is important because failure to remove excess solvent by gentle air drying may contribute to degradation of the adhesive interface overtime.
DENTIN BONDING AGENTS

Dentin bonding agents were developed to improve the adhesion between dentin and composite resin. Since dentin consists of 70% hydroxyl-apatite, collagen network, and dentin tubuli containing liquid, adhesive system with its surface treatment had been modified overtime to increase their adhesion properties.

Total-etch adhesive system

In early 1980s, Nakabayashi et al found that following acid etching and water rinsing, the mineral phase of dentin was removed but was replaced by resin during resin infiltration. Total-etch technique can demineralize enamel as well as dentin and can open dentinal tubuli to improve bond strength by creating impregnated resin tags. The new surface was either dentin and resin called hybrid layer. The hybrid layer is very strong and tough when properly formed and affords enormous micromechanical retention for resin composite bonds. Kanca et al. developed a new technique of dentin bonding agent called wet or moist bonding technique that if one's leaves some residual water in acid etched dentin, the bond strength could be doubled. Water is also an essential component because it provides hydrogen ion that are necessary for demineralization.

Self-etch adhesive system

Reduction of number of application steps should reduce manipulation time and abate technique sensitivity. This trend in adhesive dentistry has led to the introduction of self etch adhesives, of which the one step self etch adhesives. Self-etch adhesives were introduced to overcome the water sensitivity of total-etch adhesives during adhesive infiltration into the moist etched dentin. While the self-etching adhesive attacked the dentin, the resin infiltrated simultaneously into it, reducing water sensitivity. Their application procedure involves a single step of combining etching, priming and bonding. This self-etch are user friendly, less technique sensitive than total-etch which often cause postoperative sensitivity. Van Meerbeek, et al. have proposed a classification of contemporary adhesives, base on the adhesion strategy and application procedure. In general, total-etch adhesives have been found to perform better than self-etch adhesive.

Armstrong et al. reported that both hydrolysis of collagen matrix and or the degradation of the synthetic components of hybrid layer are two important factors contributing to the degradation of resin-dentin bonds overtime. Hydrolysis is a major problem affecting the bond durability of self-etching adhesives, especially their simplified version called “All-in-one” adhesives or 7th generation bonding. All-in-one adhesive contains high amount of solvent (water, acetone or ethanol) and hydrophilic monomer such as 2 hydroxyethyl methacrylate (HEMA), butylated hydroxytoluene (BHT), bisfenol glycidyl methacrylate (bis-GMA). The main difference between total-etch and self-etch adhesive is the liquid acidity. The phosphoric acid used in the total-etching is much more chemically aggressive(pH 0.1-0.6) than the self-etching adhesive(pH 2.5-4.5). As a result, etching depth induced by self-etching adhesive is usually

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Dries quickly</td>
<td>Evaporates quickly after being dispensed; can evaporate from container; sensitive to wetness of dentin; multiple coats may be required; offensive odor</td>
</tr>
<tr>
<td>Ethanol/water</td>
<td>Evaporates less quickly; less sensitive to wetness of dentin Extra drying time</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>Slow evaporation, not sensitive to wetness of dentin</td>
<td>Long drying time; water can interfere with adhesive if not removed</td>
</tr>
<tr>
<td>Solvent free</td>
<td>No drying, single coat</td>
<td>Higher film thickness</td>
</tr>
</tbody>
</table>

Table 1. Advantages and disadvantages of primers with various solvents in adhesive system

Jaya and Eriwati: Effect of surface treatment on adhesion to dentin Jurnal PDGI 61 (1) Hal. 35-42 © 2012
lower than total-etch. However, so far the simplified system do not bring the expected improvement in bonding effectiveness, in spite of their assumed reduced technique sensitivity.  

**Self adhering flowable composite**

In 2009, a new innovation in adhesive system was introduced with a significant development combination of resin technology of composite and adhesive into one product known as Self Adhering Flowable Composite. This product does not require adhesive’s material separately and contains Glycerol Phosphate Dimethacrylate(GPDM) adhesive monomer. GPDM is an adhesive monomer that has acidic phosphate functional group for etching and bonding to tooth structure. It also has two methacrylate functional groups for copolymerizing with other methacrylate monomers to form cross-linked polymeric network and to provide increased crosslinking density and enhanced mechanical strength for polymerized adhesive.  

The bonding mechanism of this self adhering flowable composite consists of two ways: firstly through the chemical bond between the phosphate functional group of GPDM monomer and Calcium ions of the tooth; and secondly through a micromechanical bond as a result of an interpenetrating network formed between the polymerized monomer and collagen fibers (as well as the smear layer) of dentin.  

Self adhering flowable composite consists of 4 types of fillers: a prepolymerized filler, a 1μ barium glass filler, a nano-sized colloidal silica, and nano-sized Ytterbium Fluoride with average particle size of 1 μ. The prepolymerized fillers (PPF) enhance the handling characteristic of the material, making it smooth and easy to manipulate. Furthermore, PPF helps minimize shrinkage due to its pre-shrunk material. Nano particles help enhance the polishability of the material and also achieve a

---

**Table 2. Components and characteristic of fourth, fifth, sixth and seventh-generation bonding agent**

<table>
<thead>
<tr>
<th>4th Generation</th>
<th>5th Generation</th>
<th>6th Generation</th>
<th>7th Generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid, primer, adhesive</td>
<td>Phosphoric acid, primer-adhesive</td>
<td>No etching with Phosphoric acid</td>
<td>No etching with Phosphoric acid</td>
</tr>
<tr>
<td>Multiple component, multiple step</td>
<td>Single component, multiple step</td>
<td>Multiple component, multiple step</td>
<td>One bottle-no mixing required</td>
</tr>
<tr>
<td>Smear layer totally lost</td>
<td>Smear layer totally lost</td>
<td>Smear layer modified</td>
<td>Smear layer modified</td>
</tr>
<tr>
<td>Rinsing required</td>
<td>Rinsing required</td>
<td>Rinsing not required</td>
<td>Rinsing not required</td>
</tr>
<tr>
<td>Postoperative sensitivity</td>
<td>Postoperative sensitivity has been reduced</td>
<td>No postoperative sensitivity</td>
<td>No postoperative sensitivity</td>
</tr>
<tr>
<td>Useful for direct and indirect applications</td>
<td>Useful for direct applications with light cure restorative material</td>
<td>Useful for direct and indirect applications</td>
<td>Useful for direct applications with light cure restorative material</td>
</tr>
<tr>
<td>Examples: all Bond II, optiBond, pro Bond, Scotchbond MP, Bond it</td>
<td>Examples: PQ1 (Ultradent), Single bond(3M), Excite, OptiBond solo(Kerr),</td>
<td>Examples: Clear fill SE Bond(Tokuyama), Liner Bond II</td>
<td>Examples: iBond (Heraeus Kulzer), One Up Bond F (Tokuyama)</td>
</tr>
</tbody>
</table>

**Figure 2. GPDM structure.**  

---

**“GPDM” Adhesive Monomer**

---

**Figure 2. GPDM structure.**
special rheological property. Ytterbium Fluoride acts as a fluoride-releasing agent (1 day → 0.23 ppm, 1 week 0.48 ppm). This new material can act as both a bonding agent and a flowable composite. In order to modify the smear layer the self adhering flowable composite starts out very acidic (pH 1.9) and neutralized (pH 6.5-7) itself upon polymerization.

Self Adhering Flowable Composite was categorized as microhybrid composite material because of the 70% filler's by weight and 48% by volume composition. It is indicated for small class I and base/liner class I and II restoration, pit and fissure sealant, repair enamel defect, blocking undercuts, minor occlusal buildups in non stress bearing areas, incisal abrasion, and porcelain repairs.

It was also reported that this material offers high bond strength, high mechanical strength and other physical attribute comparable to traditional flowable composite. However, this new material has limitation to liner or even just as pit and fissure sealant considering to the same consistency as flowable composite. Despite the one step combination of composite and adhesive system and its indication, self adhering flowable composite materials show us promises that development of new adhesive technology is growing faster or can assume this all-in-one new materials as the 8th generation bonding system.

Researchers reported that total-etch technique still have the higher bond strength than self-etch and self-adhering flowable composite because of the more chemically aggressive (pH 0.1-0.6) than the self etching adhesive (pH 2.5-4.5) and self adhering flowable composite which starts out very acidic (pH 1.9) and neutralized (pH 6.5-7) upon polymerization. However, total-etch often showed more sensitivity when applied in dentin or near pulp. Self etch technique can be used to reduce post operative sensitivity near the pulp. Self-adhering-flowable composite have the potential to simplify our procedures and inventory of product, but they must perform up to level of more conventional bonding agent/restorative combination. Therefore, dentist must know the character and ways of working on material adhesive to achieve long lasting composite resin restoration.

It can be concluded that the different strategy on surface treatment in total-etch, self-etch and self-adhering flowable composite which remove smear layer (total-etch) and maintain smear layer as substrate (self-etch, self-adhering flowable composite) resulted different bond strength. Dentist must have the ability to choose the appropriate material in utilizing adhesive material for their patient cases. The properties and composition of adhesive products must be reviewed properly especially for its indication, manipulation and application techniques for successful restoration.

REFERENCES


