Review Article

Biodegradation of Dentin-Resin Adhesion and the Prevention: A Systematic Review

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Abstract

Composite resin is a tooth-colored restorative material with aesthetic and highly desirable. However, this restorative material may change slowly due to degradation. Degradation of composite resins structures is caused by mechanical processes such as sliding, abrasive, and fatigue and chemical processes such as beverages, food, microorganism and hydrolytic enzyme or catalyst containing saliva. Degradation may involve particle fillers, coupling agents and matrix. Various strategies have been implemented to extend the life of the composite resin adhesion to the tooth structure, including the use of ethanol wet bonding and applications of chlorhexidine as an inhibitor of matrix metalloproteinases (MMP's). Thus, remineralization appears to be the cognitive approach for extending the longevity of resin-dentin bonds. Guided tissue remineralization recaptures the hierarchical order and dimension of apatite crystals of normal mineralized collagen. It represents a revolutionary approach to improve the durability of resin-dentin bonds using a particle-mediated, non-classical crystallization strategy. This paper presents an overview of contemporary strategies for preventing degradation of resin-dentin bonds and provides an evaluation of their applicable foreground on the durability of resin-dentin bonds.

Keywords: Biodegradation; Composite resin; Dentin-resin adhesion; Prevention

Introduction

Composite resin restorative material is the most widely used materials for the dentist and patient today. This is because the value of the esthetic result produced by the restorative material is very satisfying. In addition, composite resin restorations produce a good bond to the surface of the enamel or dentin [1]. Composite resin material was first discovered in 1951 by Knock and Glenn. Since then, the composite resin restorative materials continue to grow until now. In 1962, Bowen expanded the material by adding material bisphenol glycidyl dimethacrylate (bis-GMA) that play a role in strengthening the chemical bonds between composite resin filler particles. Until now, all kinds of resin composites contain bis-GMA [2,3].

Although composite resin material produce good aesthetic, shape but surface of composite resin restorations can change over time. This will affect the mechanical properties of the composite resin. The process of this change is known as composite resin degradation. Degradation of composite resins is the missing or releasing chemical structure of composite resin such as Bis-GMA due to some processes [1]. This degradation causes the damage of the restoration and eventually resulting in the non-durable restoration. The mechanical properties of composite resins are not only influenced by its containing chemical structure but also influenced by environmental conditions such as pH changes and oral cavity humidity [4].

Failure of dental restorations is a major concern in dental practice. Up to half of all composite resin restorations failed within 10 years. A randomized clinical trial for the past 7 years has shown that the risk of secondary caries was 3.5 times greater in the composite resin compared to amalgam restorations. This explains the reason of taking an effort to extend the life of the resin composite restoration [5].

According Ferracane, et al. (2006) and Goperfich, et al. (1996), composite resin degradation mechanisms associated with the two processes of mechanical and chemical processes. Causes of mechanical processes such as sliding, abrasive, and fatigue meanwhile composite resin degradation due to chemical processes caused by hydrolysis enzymes or saliva containing catalysts [1,2]. Various strategies have been implemented to extend the life of the composite resin adhesion to the tooth structure, including the use of ethanol wet bonding and applications of chlorhexidine as an inhibitor of matrix metalloproteinase [6].

The purpose of this paper is to investigate the degradation of resin composite restorative materials used in dentistry includes definition, etiology and mechanisms, as well as the prevention of degradation of resin composite. In this paper, it is also described about the adhesion of composite resin and factors that affect adhesion of composite resin to the tooth structure.

Composite resin

By definition, composite is a material consisting of two or more components. Resin composites are complex materials, which generally consist of organic components (resin) that form the matrix, inorganic filler material, interfacial materials to unify the resin and filler, initiator systems to enable hardening or polymerization mechanism, stabilizers (inhibitor) and pigments. Organic components (resin) and inorganic components (filler) are incorporated into a system that will affect the polymerization. Usually the filler particles are coated

Tabel 1: Advantages and disadvantages of several types of solvents.

Solvent	Advantages	Disadvantages
Acetone	Dry quickly	Evaporate quickly, sensitive to moist dentin, more layering needed
Ethanol	Less evaporation, less sensitive to moist dentin	Dry quickly
Water	Slow evaporation, less sensitive to moist dentin	Long drying time, water can give negative effect to the adhesive
Solvent-free	Hard to get dry, one layering	High thickness

with a binding agent to link the organic components (resin). Most of the resin matrix containing aromatic monomers with high viscosity which is bis-GMA (bisphenol-A diglycidyl dimethacrylate) that synthesized by Bowen in the USA in 1960. Low viscosity monomer is also incorporated in them, such as TEGDMA (Triethylene Glycol dimethacrylate), EGMA (Ethylene Glycol Dimethacrylate) and HEMA (Hydroxyl-Ethyl Methacrylate) [1-3].

Adhesion mechanism of composite resin

An effort to improve the adhesion of composite resin to dental tissue is the use of acid etching and adhesive bonding material. Buonocore, et al. (1955), introduced the concept of bonding with the acid etching that modifies the enamel demineralization using acidic agent.2 The process of acid etching on enamel surface will produce microscopic roughness on the surface called the enamel tags or micropore in order to obtain a physical bond between resin composite and enamel that creates micromechanical retention . The success of these efforts has led researchers to apply etching on dentin, but though the dentin is etched but composite resin adhesion to dentin surfaces is harder than the adhesion of the enamel surface. The difficulty is because dentine constitutes more complex tissue than enamel [2].

Enamel is an almost complete mineralized tissue, while dentin is a living tissue that consists of inorganic component (45%), organic components (33%) and water. Organic composition of dentin substrate has structure of ultra tubules and heterogeneous. Thus, it can be said that the factors influencing adhesion difficulties of composite resin on the dentin is the variation of mineralization rate and the presence of fluid in the dentinal tubules that hinders the adhesion. [2,3].

The mechanism of composite resin adhesion on dentin depends on the number of smear layer. Smear layer is a layer of inorganic debris on the surface of dentin because of preparation. Smear layer is expected to produce a barrier that protects the pulp from the damaging pulp stimulation, but its function is only temporary. To overcome this, dentin etching is done remove the smear layer. Fusayama, et al. (1980) reported that dentin etching will form a micromechanical adhesion between dentin and resin composite as well as to dissolve the smear layer [2].

Smear layer removed by etching with phosphoric acid 35 -37% for 15 seconds which leads to the opening of dentinal tubules. Etching of the intertubular and peritubular dentin resulted in penetration and adhesion for bonding material to form the hybrid layer. Hybrid layer is the enamel, dentin and cementum which are infiltrated by the resin [1,2].

Basically dentin bonding system consists of three components, namely:

a. Etchant: Acid etching leads the tooth surface etched with an acidic substance into roughness. Etchant can increase microscopic roughness through decalcification of enamel surface by removing the prismatic and interprismatic mineral crystals. In addition, etchant can also improve the enamel surface free energy to produce enough resin monomer infiltration as the retention of composite resin restorations, dentin surface decalcification by dissolving the hydroxyapatite crystals of the peritubular and intertubular dentin in order to open dentin tubules so that fibers and collagen in the intertubular dentin will be exposed to monomer infiltration (in a total-etch adhesive system) or modify the smear layer (the self-etch adhesive systems) [1,2].

b. Primer: Primer is a hydrophilic low viscosity monomer. This causes the material is easy to adapt to the dentine surface which is also hydrophilic. Priming process produces a chemical bond, the intermolecular interaction between carboxyl or phosphate groups of primer with collagen (in a total-etch adhesive system) or hydroxyapatite crystals which covers the collagen (in self-etch adhesive system). Adhesive is usually available in the form of a solution with 60-80% solvent such as: BPDM / HEMA, HPDM / NTG-GMA, 4 META / MMA, glutaraldehyde [1,2].

c. Bonding agent (adhesive resin): Adhesive resin is generally hydrophobic and is compatible with primer and resin composites. Polymerized resin adhesive attached to collagen fibrils (total-etch system) and the remaining of hydroxyapatite crystals (the self-etch systems) produces interfacial structures called "hybrid layer"[1,2].

Factors affecting the adhesion between resin and tooth structure

Adhesion to the tooth surface is affected by several factors, namely:

a. Operator: The successful adhesion of restorative material to the tooth surface depends on the operator technique, such as restoration techniques that require proper isolation of the work area, good manipulation, procedure of etching and bonding, layering technique of insertion, the shaping and polishing of restoration [2,6].

b. Material: There are different types of restorative materials that utilize different application procedures. With total etch adhesive system, composite resin material relies on phosphoric acid etching procedure to the tooth surface. Phosphoric acid etching is used to remove the rest of the cement, smear layer, dentin which contains eugenol and demineralized dentin [2,6].

c. Tooth structure: Dentin has high water content. This causes the failure of resin adhesion to peritubular hydroxyapatite and dentin organic material produces lesser hydroxyapatite so making it less resistant to acid. Demineralized hydroxyapatite has poor quality because it can not form resin tags [2,6].

d. Effect of solvent: Solvent has a role to elevate water from the dentin surface that provides a reaction between dentin and the hydrophilic adhesive. According Perdiago, et al (2001), the strength of the dentin bonding done with repeated humidification depends on the type of solvent in a humidification system and re-humidification time. Here are the advantages and disadvantages of the material on the system solvent adhesive (Table 1) [2,6].

Degradation of composite resin adhesion

Degradation of composite resins is the missing or release chemical composition of resin composite structures caused by some processes namely mechanical and chemical processes. Degradation of resin composite restorations may be resulted from damaged and ultimately becomes not durable. Degradation of resin composite restorations alters the microstructure of the surface by forming pores or small holes. The pores are caused by missing or loss of composite resin content such as filler particles and matrix [1,2].

According Ferracane (2006) and Goperfich (1996), composite resin degradation mechanisms are associated with the two processes of mechanical and chemical processes. Causes of mechanical processes such as sliding, abrasive, and fatigue while the chemical process is caused by hydrolysis enzymes or saliva containing catalysts [1,2].

Chemical process: Composite resin degradation due to chemical processes are influenced by various factors, including molecules diffusion and speed of molecules reaction, food particles, and fluid that removes corrosion from the surface of the polymer. In other words, the diffusion properties of resin composite especially resin matrix has role in the process of chemical degradation. Resin composition, degree of conversion, the bond between matrix and filler particles, as well as the filler volume also affect chemical degradation. In addition, it is also influenced by environmental conditions of the oral cavity, such as beverages, food, microorganisms and saliva (Figure 1 and Figure 2). These components may alter molecules diffusion resulting in the bubbles of resin matrix that can change the speed of degradation [2].

Saliva can cause degradation of composite resin. It is influenced by the composition and viscosity of saliva itself. In addition, the enzyme can also cause degradation of composite resin. Enzymes are formed by inflammatory cells such as salivary esterase, cholesterol esterase, pseudocholinesterase, and acetylcholinesterase can also dissolve the polymer [2].

Composite resin consists of filler particles bonded to the resin matrix via coupling agent, therefore chemical degradation that occurs involving the chemical structure of the composite resin which is degradation of the filler particles, degradation of the filler-silane and degradation of the matrix [2].

Degradation of filler particle caused by chemical processes in the oral cavity. One of the chemicals is saliva that has high water content. Saliva can cause hydrolytic damage of filler surface. Damage is caused by two mechanisms. The first mechanism is the release of the filler element. After the water diffuses through the matrix and reaches the filler particles surface, water damages the glass surface and finally the fillers surface become damaged. Glass that exposed to water will release of sodium ions and replaced by hydrogen ions from water. Hydrogen ions are smaller than sodium ion so that the glass surface

will receive a tensile stress. Hydrogen ions are absorbed by glass surface then the concentration of hydrogen ions increases on the glass surface [2].

When the water reaches pH 9.5, OH-ions will break siloxane bonds on the glass surface. Throughout the process, siloxane is still absorbing hydrogen ions. The destruction process of siloxane bonds results in the formation of new compounds of SiOH and OH-ions that involve in further destruction of siloxane bonds. Reaction becomes autolytic because OH-ions that play its role in the destruction of siloxane bonds are also used in the further destruction of other siloxane bond. Autolytic reaction caused the glass to be weakened [2].

The degradation mechanism of the second filler is the reaction between the filler particles and fluoride components. Particularly the use of fluoride gel may stimulate changes in the composite resin surface. The changes are caused by degradation of filler material, debonding and loss of filler particles. The mechanism is based on the interaction between fluoride ions with the silicon atoms of the silica structures. When a reaction occurs, the siloxane bond is broken and the hydrogen ions react with SiOH into SiO- [2].

A very important component in the composite resin material is coupling agent. This material usually consists of Methacryloxy Propyltrimethoxy Silane (MPS). Silane will react with the surface of the filler material to form siloxane bonds. Siloxane bonds can have failure caused by two mechanisms. The first mechanism is due to degradation of the bond between silane materials and filler particles. Surface of filler material degraded so that coupling agent will instantly receive pressure. This process led to the release of siloxane bonds. The second mechanism is the enzymatic degradation of silane molecule itself. This is due to silane molecules that do not bind to the filler. In other words silane molecules undergo natural hydrophobia against filler particles [2,4,7].

Degradation of the matrix is influenced by the curing degree or irradiation. The increase of curing degree will affect the degradation of the filler surface by increasing the thickness of the resin and reduce the degree of diffusion through the matrix material so that the reaction on the surface of the filler material will be slow. Matrix degradation can also be caused by the heat generated during the polishing procedure. Heat to 200˚ C will cause depolymerization of methyl methacrylate-based resin to form monomers. This will result in the formation of porous and decrease of composite density. Enzymes like esterase in the oral cavity can also damage the resin bond. Research conducted

Figure 1: Composite restoration.

**Figure 2:** Degraded composite restoration.
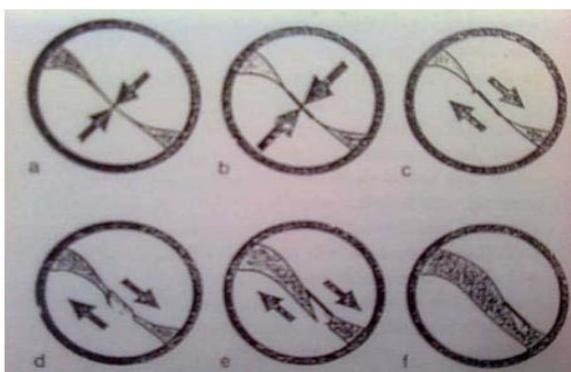
Figure 3: Composite resin degradation due to sliding process; (a) and (b) Initial contact on flat surface between composite resin restoration and adjacent tooth. (c) Friction between two flat surfaces; (d) and (e) Friction leading to degradation of composite resin restoration; (f) Degradation of composite resin resulting in non contact with adjacent tooth [3].

by De Gee, et al. (2003) states that enzymes can accelerate the damage of composite resin [2,6,8].

b. Mechanical processes: Composite resin degradation resulting from mechanical process is the most common degradation and is associated with a lack of tensile strength and hardness composite resin [5]. Mechanical degradation of resin composite is damage of composite resin restoration caused by friction or physical contact that occurs between the composite resin and teeth or with others. The mechanical degradation processes such as sliding, abrasive, and fatigue [1].

The process of sliding is friction between composite resin restoration or with other restoration. This process begins when the two flat surfaces come into contact with each other (Figure 3). Contact area will be in close contact due to pressure from both surfaces. The two surfaces contact will shift if there is pressure such as the pressure of mastication and cause friction between the two surfaces. Friction can cause damage to the weakest surface of the two surfaces. Such damage is termed as degradation [1,3].

Archard JF (1953) in his research on the degradation caused by the sliding process using a constant pressure stated that the amount of the loss of chemical structure of the composite resin material is influenced by both the surface contact area and friction distance [1].

In the process of abrasive, the loss of chemical structure of composite resin restoration is associated with the surface of composite resin comes into contact with teeth at one point or another restoration before reaching maximum occlusion. This causes the broken surface of the composite resin restoration at one point of contact. Abrasive process is a mechanical process that most often lead to degradation (Figure 4) [1-3].

Abrasive processes are also influenced by dietary factors and masticatory habits [1].

Sliding and abrasive processes are mechanical process associated with friction between two solid surfaces. While the fatigue associated with premature contacts. Tooth cusps that contact prematurely to the surface of composite resin restoration can cause damage of the restoration (Figure 5) [1-3].

Strategies for preventing degradation of resin-dentin bonds

There are several methods to prevent the degradation of composite resin adhesion to the tooth surface, namely:

Ethanol-wet bonding: Hydrophobic polymers are polymers that are prone to water absorption. This can reduce the mechanical properties of the resin. More hydrophobic resin such as bis-GMA and TEGDMA can be used to coat the collagen fibrils during resin bonding with the possibility of less water absorption and better collagen fibrils coating thereby slowing or preventing the hydrolytic enzyme catalyzed by collagen. Hence, there developed a new bonding technique called ethanol wet bonding [5,6].

There are three steps in the ethanol-wet bonding: (1) water replacement in the collagen matrix with ethanol thus making it more hydrophobic, (2) Dissolution bis-GMA/TEGDMA in ethanol to produce a relatively hydrophilic primer, and (3) primary infiltration bis-GMA / TEGDMA into the ethanol-saturated dentin. There is speculation that the mixture bis-GMA and TEGDMA able to go deep into the hybrid layer without phase change. Replacement of water by ethanol increases the bond strength of most hydrophobic resins including bis-GMA/TEGDMA mixtures by bringing the Hoy solubility parameter for δt of the ethanol-saturated matrix very close to that of ethanol-solvated bis-GMA/TEGDMA mixtures [5,6].

When bis-GMA alone was bonded to acid-etched dentin, dentin bonding exhibited bond strengths equivalent to what some academicians regard as the 'gold standard' for contemporary hydrophilic dentin adhesives. Hybrid layers created using bis-GMA are thinner, due to the intended collagen matrix shrinkage and exhibiting a similar extent of nanoleakage as might be created by hydrophilic dentin adhesives. hydrophobic monomers are immiscible with water, contamination of these resin monomers with as little as 5% of water on the ethanol-saturated dentin substrate resulted in a 25% reduction in tensile strength of the experimental hydrophobic adhesive to dentin. The use of tubular occlusion materials provides a possible solution to the problem of water re-contamination. Despite this, coaxing of hydrophobic resins into acid-etched dentin, using ethanol-wet bonding to preserve resin-dentin bond integrity can only be used for etch-and-rinse adhesives, and not for self-etch adhesives [5,6,8,9].
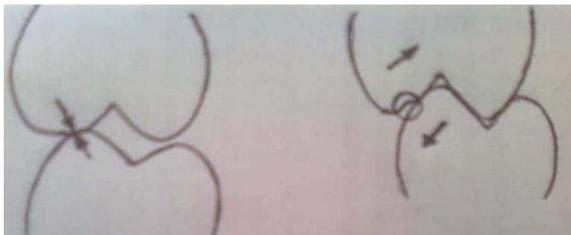
Figure 4: Degradation due to abrasive process.

Figure 5: Clinical view of degraded composite restoration due to abrasive process.

Inhibitors of matrix metalloproteinases: In the hybrid layer degradation by MMP's, MMP's inhibitors act to protect the collagen in the hybrid layer. According to Gendron et al, chlorhexidine could inhibit MMP-2, -8, -9, and even at very low concentrations while maintaining the integrity of the hybrid layer. However, chlorhexidine has only limited substantivity. The role of chlorhexidine is to delay dentin demineralization rather than to stop bonding degradation permanently. It also should be noticed that there is the zone of resin-less demineralized dentin. Chlorhexidine only works on etch and rinse adhesive, since chlorhexidine can not bind to the collagen matrix in an acidic environment [10-15].

Guided tissue remineralization: Guided tissue remineralization is a potentially new way to extend the life of the resin-dentin bonding using polianion calcium phosphate nanotechnology and biomimetic principles. When applied to the targeted tissue remineralization model of demineralized dentin, remineralization occurs with different characteristics. Remineralization on uncompleted infiltrated tissue in the hybrid layer infiltrated occurs to the density of the tissue elekron be similar to the mineralized base dentin and almost covered most of the surface of demineralized dentin [5]. Long-term results of the in-vitro bond strength with microtensile test verified that the bond strength of biomimetic remineralization group remained stable after water storage for 9 months, while the control group decreased significantly.

Mineral intrafibrillar and interfibrillar identified and led to 156-219% increase in the modulus of elasticity of demineralized dentin after 4 months of remineralization process. Examination of specimens that have been remineralized after 15 weeks showed that the reformed nanocrystal in peritubular dentin is much smaller than the adjacent intertubular dentin. Peritubular dentin contains organic matrix different from non-collagen proteins found in intertubular dentin. Organic matrix in peritubular dentin essentially without collagen but rich in glutamic acid containing protein and mass calcium proteolipid-phospholipid-phosphate complex [5].

Conclusion

In Conclusion, composite resin is a tooth-colored restorative material with aesthetic and highly desirable. However, this restorative material may change slowly due to degradation. Degradation of composite resins is missing or release chemical composition of resin composite structures caused by mechanical processes such as sliding, abrasive, and fatigue and chemical processes such as beverages, food, microorganisms, and hydrolytic enzyme or catalyst containing saliva. Degradation may involve particle fillers, coupling agents and matrix. Various strategies have been implemented to extend the life of the composite resin adhesion to the tooth structure, including the use of ethanol wet bonding and applications of chlorhexidine as an inhibitor of matrix metalloproteinase.

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