

“SUPER DENTIN”: REINFORCEMENT OF ADHESIVE-DENTIN INTERFACE AND PROTECTION OF TOOTH STRUCTURES

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ABSTRACT

Dentin has a limited potential to resist an acid attack of secondary caries. Even after the restoration of carious lesion leakage at the interface between restoration and tooth was a frequent problem which lead to secondary caries. Dentin bonding systems have been dramatically simplified and improved during the recent decades. Monomer penetration into dentin and its polymerization creates a hybrid layer, which is essential to obtain good bonding to dentin. Diffusion of acid monomer beyond the classic hybrid layer and their ion exchange interactions with the hydroxyapatite results in formation of stable organic complexes and this modified dentin is termed as

‘Super Dentin’ with superior resistance against caries activity created by the use of self-etching adhesive resins. Acid base resistance zone is formed beneath the hybrid layer with a self-etching primer adhesive system, considered to be due to the monomer penetration potential and fluoride release in the adhesive systems. Natural dentin has a limited potential to resist an acid attack of secondary caries; however, the acid base resistant zone does not purely consist of dentin in morphology, it is rather a combination of dentin and the adjacent hybrid layer. Therefore, the reinforced dentin has been called ‘Super Dentin’ bearing the ability to prevent primary and secondary caries. Prospectively, the great potential of adhesive technology in creation of the ‘Super Dentin’ would lead to the development of new materials for mechanical, chemical and biological protection of the dental structures. This review article demonstrates detail in ‘Super Dentin’.

KEYWORDS: Acid Base Resistance Zone, All in One Adhesive System, 10-Methacryloyloxydecyl Dihydrogen Phosphate.

INTRODUCTION

Dentin has a limited potential to resist an acid attack of secondary caries. Microleakage at the interface between restoration and tooth is a frequent problem which leads to development of secondary caries. Secondary caries has been defined as “lesions at the margins of existing restorations” or “caries associated with restorations or sealants”. Secondary caries is a complex, multifactorial process, interweaving the various causes of same as primary caries with the varies characteristics with type of restoration and restorative material involved, i.e., secondary caries pathogenesis follows the same concept for any other caries lesions, involving demineralization and, in case of dentin secondary caries, enzymatic dissolution of the organic component, but is modified by the presence of a restoration or sealant margin. Secondary caries may be associated with a defective restoration mainly via gaps between the restoration and the tooth allowing acidic fluids or biofilm to enter the interface or associated with an intact restoration e.g., via a lower buffering capacity of the restoration compared with the tooth hard tissue or because of presence of primary caries adjacent to existing restorations (mainly when the caries process has not been sufficiently addressed on a patient level and the surface next to the restoration becomes carious as a result of this ongoing caries activity).^[1] The known factor relevant for caries development is presence of a cariogenic biofilm, supply with fermentable carbohydrates, imbalance in mineral loss, and loss of dental hard tissue. A number of in vitro studies, using various secondary caries models, have been performed, yielding threshold gap sizes of the defect between 60 and 1000 μm .^[2] Diffusion of acid monomers beyond the classic hybrid layer and their ion exchange interactions with the hydroxyapatite results in formation of stable organic inorganic complexes and prevent secondary caries. This paper has reviewed the previous studies on assessment of ultrastructure of the acid base resistance zone (ABRZ) at the adhesive-dentin interface also, the mechanism of the ABRZ formation and a new concept of “Super Dentin”.

Super dentin

Super dentin is modified dentin of combination of dentin and the adjacent hybrid layer with superior resistance against caries activity created by the use of self etching adhesive resins. Dentin bonding systems have been dramatically simplified and improved during the past decades. A hybrid layer is created after monomer penetration into dentin and its polymerization in situ, which is needed to obtain good bonding to dentin.^[3] Theoretically, Marginal sealing of the cavity and resistance against acid challenge to prevent secondary caries can be provided by the hybrid layer.^[4] However, it was reported that none of the

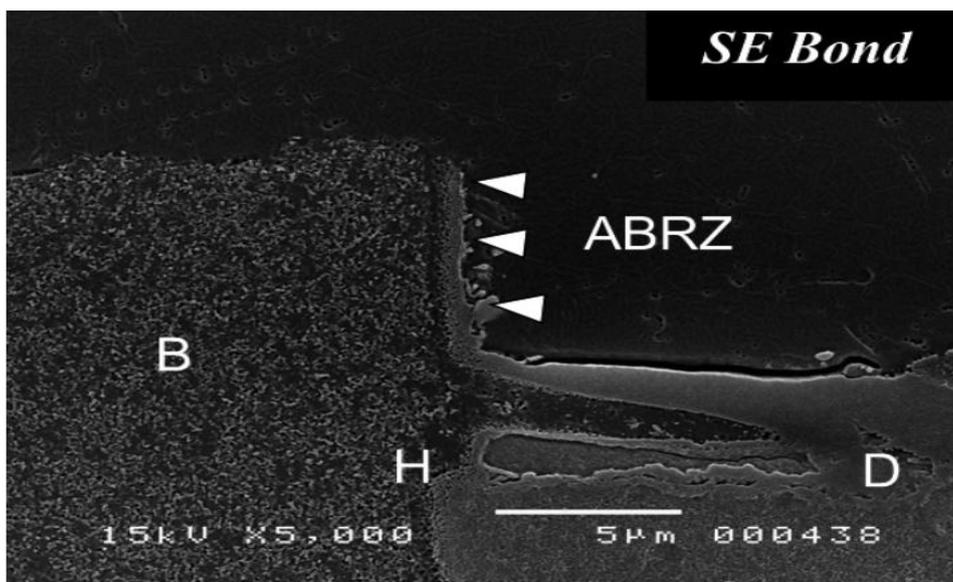
adhesives currently available could completely eliminate nanoleakage along the dentin-restorative interface. The concept of minimal cavity preparation has become widely accepted for the placement of direct composite restorations by using an adhesive system. But recurrent caries is still considered to be one of the major reasons for failure of resin composite restorations. Tsuchiya *et al.* observed artificial secondary caries inhibition around restorations bonded to bovine root dentin, using an SEM.^[5] A new zone, named, “acid-base resistant zone” (ABRZ), was found beneath the hybrid layer in SEM observation, which was completely different from the inhibition zone formed due to release of fluoride from materials such as a glass ionomer cement; also, the acid-base resistant zone was formed in spite of the fluoride-free adhesive.^[5] It has been shown that thickness of ABRZ is between 500 -1000 nm. Nikaido *et al.* have referred to the ABRZ as “super dentin.

Mechanism of action of formation of super-dentin

Nakabayashi *et al.* proposed hybridization concept as a dentin bonding mechanism.^[3] In this concept, monomer penetration into dentin and its polymerization *in situ* creates a hybrid layer, which is believed to be essential for good dentin bonding. ABRZ was found beneath the hybrid layer. The formation of ABRZ has been confirmed only with a self-etching system, but not with an acid-etching system.^[6] The self-etch adhesive systems demineralize dentin mildly and partially, leaving hydroxyapatite crystals in the base of the hybrid layer. Such residual apatite crystals may serve as a template for additional chemical reaction with the functional monomer. Among the functional monomers, 10-Methacryloyloxydecyl dihydrogen phosphate (MDP) is known to have a high chemical bonding potential to hydroxyapatite forming a very stable bond and excellent water resistance confirmed by the low dissolution rate of its calcium salt in water. When the dentin surface is aggressively etched with phosphoric acid, the underlying dentin may become completely demineralized so deep that hydroxyapatite in the underlying dentin would disappear and the bottom of the demineralized dentin would be inaccessible to complete impregnation by the resin. In this case, a functional monomer may not have the opportunity to react with hydroxyapatite at the base of the hybrid layer, resulting in lack of the ABRZ formation with an acid-etching system. If the ABRZ is assumed made of resin-infiltrated dentin, the same chemical reaction of hydroxyapatite and an acidic monomer in the adhesive may take place in this zone, giving rise to the ability to resist against demineralization from an acid attack from the microorganisms in primary and secondary caries. Therefore, the reinforced dentin was proposed to be called as Super Dentin, which should be superior to the normal dentin mechanically, chemically, and biologically.^[6]

Formation of the ABRZ was strongly influenced by the fluoride ions released from a fluoride-containing adhesive system, which may accelerate remineralization reaction of dentin against acidic challenge, and create thicker ABRZ, compared with a fluoride-free adhesive system.^[7]

We know that incorporation of fluoride into hydroxyapatite can result in formation of fluoroapatite, which has a higher resistance to acid. However, the existence of the ABRZ should be a different phenomenon than solely reinforcement by fluoride release. In fact, while fluoride has a positive effect on ABRZ formation, the zone is originally considered to be associated with adhesive monomer penetration deeper than previously expected. The exact mechanism is not understood yet; however, there is mounting evidence that the acidic moiety (carboxylic or phosphate group) of the functional monomers in some self-etching materials could interact with the calcium of hydroxyl apatite and form an ionic bond.^[8] It was reported that the chemical bonding of the acidic monomers to dentin and enamel could result in formation of tooth with increased resistance against demineralization by acids and therefore resistance to caries. One of the most successful acidic monomers in the composition of self-etch systems is 10-Methacryloyloxydecyl dihydrogen phosphate (MDP; Kuraray Medical, Tokyo, Japan), with a C=C bond on one end for polymerization and a reactive acidic moiety on the other end as in.^[8] Under transmission electron microscopy (TEM), selected area electron diffraction (SAED) is a crystallography method that provides information on the local crystalline structure of thin sections. The TEM/SAED evidence demonstrated that the ABRZ contained densely arranged apatite crystallites that had different characteristics from the hybrid layer.^[9] Using the self-etching technology, formation of “Super Dentin” may become a key strategy in preventive dentistry in the future. Root surface coating with the dentin bonding systems is considered to be an effective measure for protection against caries, erosion and abrasion.^[10] providing a strong physical barrier with the formation of ‘Super Dentin’.



SEM image of the dentin-adhesive interface after acid-base challenge. The acid-base resistant zone (ABRZ) was observed beneath the hybrid layer in a two-step self-etch adhesive system (5000X magnification).

Super dentin with different adhesive system

According to the concept and mechanism of the adhesive systems, the classification of recent bonding system can be done into two main categories: self-etching primer systems and acid-etching systems. The category of self-etching primer systems is further divided into two sub-categories: two-step self-etching primer systems and one-step self-etching primer systems, including the so-called “all-in-one adhesive systems”. Recently, universal adhesives have been introduced to the market, which can be categorized under the all-in-one adhesives in terms of their mechanism.^[11] A two-step self-etching primer system is composed of a self-etching primer and an adhesive. The self-etching primer contains one or several acidic monomers in their components that can condition and prime dentin surface simultaneously. In the one-step adhesive systems, the roles of the self-etching primer and the adhesive are combined into one application step.^[6]

The category of acid-etching systems contains conventional acid-etching systems, three-step etching/priming/bonding systems. Current acid-etching systems usually use 30-40% phosphoric acid, which removes the smear layer from a prepared dentin surface, which demineralizes dentin and exposes the collagen fibrils over a depth of 3–5 μm.^[18] Therefore, phosphoric acid etching results in severe demineralization of dentin surface when compared

to the self-etching systems. Milder form of phosphoric acid have a pH of around 2.0 and higher.^[11]

Super dentin with all-in-one adhesive system

To simplify the bonding procedures, all-in-one adhesive systems have been developed and commercialized. All-in one adhesives contain acidic monomers, water, and solvents in order to create a bond between tooth substrate and resin composite by a single step. These systems have advantages for clinicians in saving time. However, the adhesive resin layer of the all-in-one adhesives is permeable and allows the formation of a water channel or water tree.^[12] Two well-known examples for these systems are Clearfil Tri-S Bond (Kuraray Medical) and G-Bond (GC Corp., Tokyo, Japan). They both are fluoride-free all-in-one adhesive systems, which contain acidic monomers of 10-Methacryloyloxydecyl dihydrogen phosphate (MDP) and 4-methacryloxyethyl trimellitate anhydride (4-META), respectively. Acidic monomers play roles to condition and prime dentin simultaneously. The acidity of these adhesive systems did not reach that of the etchants in the acid-etching systems, such as phosphoric and citric acids.^[13] So, all-in-one adhesive systems demineralize dentin partially, leaving mineral crystals in the hybrid layer. For Clearfil Tri-S Bond and G-Bond the thickness of both adhesives was less than 10 mm. It was observed approximately 1 mm thick ABRZ beneath the hybrid layer, for both materials. In all-in-one adhesives, hydrophobic and hydrophilic resin components are intermixed prior to polymerization. Phase separation can occur as the solvent alcohol or acetone is evaporated. The larger portion of adhesive solvents is removed by air drying after adhesive application, but residual water still persists due to lowering of the vapour pressure of water by 2-hydroxyethyl methacrylate (HEMA). Knowing that monomers can infiltrate deeper than the hybrid layer, and that water inhibits polymerization of the adhesives. So it is possible to speculate that a weak area beneath the hybrid layer and ABRZ may be created, which is partially demineralized, while the penetrated monomers are not completely polymerized,^[14] due to the phase separation and water existence. In contrast to the ABRZ, it is reasonable to assume that this area is probably more vulnerable to acid challenge, resulting in the formation of typical erosion areas beneath the ABRZ in some adhesive systems.^[15]

Super Dentin with acid etching adhesive system

Initially it was thought that the ABRZ may be specifically formed below the hybrid layer of adhesives that do not require acid etching of dentin. In order to probe this speculation and

further clarify the attributes of this zone, Takagaki *et al.* evaluated the ultrastructural change of the adhesive-dentin interface after acid-base challenge using an acid etching adhesive system, 4-META/MMA-TBB resin with three different conditions.^[16] Super Bond C&B is methylmethacrylate (MMA)-based, and contains a chemical initiator of a tri-*n*-butyl borane (TBB) derivative and a functional monomer of 4-methacryloxyethyl trimellitate anhydride (4-META), giving an excellent adhesion to dentin, when dentin surface is pretreated with citric acid solution containing ferric chloride.^[17] The dentin surfaces received one of the following pretreatments: no treatment, 65% phosphoric acid for 10 s or 10% citric acid and 3% ferric chloride for 10 s. After application of phosphoric acid or 3% ferric chloride, the dentin surfaces were rinsed with water and gently air-dried. The mixture of liquid and powder of Superbond C&B was applied on dentin surface with a brush-on technique according to the manufacturer's instructions to bond a PMMA rod. The bonded specimens were left at room temperature for 30 min to secure the initial polymerization, and then stored in distilled water at 37°C for 24 h. In the no treatment group, the hybrid layer was not created at the interface, however, wall lesion was observed along the interface. Formation of the hybrid layer was observed in both the ferric sulphate and phosphoric acid groups; however, no detection of ABRZ in any of the groups. Nevertheless, without surface conditioning, 4-META/ MMA-TBB resin could not bond to dentin, because smear layer on the ground dentin surface prevented monomer penetration into underlying dentin. In the SEM observation after acid-base challenge, no hybrid layer formation was observed. Formation of wall lesion suggested that the interface without hybrid layer could not resist against acid-base challenge, indicating that a dentin margin without a hybrid layer would suffer secondary caries in the oral environment. The hybrid layer was recognized in both ferric sulphate and phosphoric acid. However, thickness of the hybrid layer with phosphoric acid was 2 mm, while thickness with the 3% ferric chloride was 1 mm because of different acidity in two solutions. Based on the results of the previous studies an ABRZ was formed beneath the hybrid layer with a self-etching primer adhesive system. The ABRZ was not observed in the acid-etching system.^[16] So it was suggested that the existence of the ABRZ could be related to monomer penetration into the partially demineralized dentin, only when a self-etching primer adhesive system was used.

Clinical application

Thin-Film coating materials

The resin coating technique is applicable to both anterior and posterior bonded restorations. However, the combination of a dentin bonding system and a low-viscosity micro-filled resin creates a thick coating layer on the dentin surface.^[18] Thickness of the cured dentin bonding agent can vary significantly according to the composition of adhesive system and also surface geometry.^[19] A thick coating is not suitable especially for a crown preparation because of the possibility of deformation of the preparation by the resin coating. But the all-in-one adhesive technology provides a thin film coating, less than 10µm in thickness on the dentin surface. An all-in-one adhesive with mild acidity has already been marketed for use as a desensitizing agent for the hypersensitive dentin. Such coating materials are clinically accepted for sealing the exposed dentin of the crown preparation. The thin-film coating material demonstrated to improve the dentin bonding performance of resin cement and prevent marginal leakage beneath the restorations.^[20] However, the combinational method of applying a dentin bonding system and a flowable resin composite still provides more reliable dentin bonding performance than the thin-film coating alone.

Application of resin coating to the endodontically treated teeth

The resin coating technique can be applied not only for the preparations of vital tooth but also for root canal dentin of the endodontically treated tooth. The goal of endodontic obturation is to provide an effective apical seal to prevent bacterial invasion from the oral cavity through the root canals. The apical seal can be adversely affected by coronal leakage once the coronal restoration is lost or becomes defective. Dissolution of the sealer allows access of periapical fluids, and bacteria into the root canal. Fractured teeth and leaking/lost temporary restorations are often encountered clinically, which can leave the root canal filling open to the oral cavity. Therefore, the quality of the coronal seal is very important for the ultimate success of any root canal obturation. The application of a resin coating to the coronal opening of the endodontically treated tooth could minimize coronal leakage.^[21] Perfect sealing was achieved by coating with a combination of a self-etch adhesive and a flowable resin composite. For successful adhesive restorations of non-vital teeth, it is important to obtain good dentin bonding to endodontically treated dentin. Ariyoshi *et al.* (2008) demonstrated that resin coating significantly enhanced the microtensile bond strengths of indirect composite cores to pulpal floor dentin.^[22]

Surface coating for tooth structure preservation

Sealing of pit and fissure of occlusal enamel with composite resins has been widely accepted to prevent enamel caries in children and adolescents. Nowadays, preventive concept approaches expand to smooth enamel surfaces. In order to protect enamel from dissolution, the superficial penetration and surface coating of the adhesive and/or caries infiltrate is considered as one of the most optimal treatment options. The MDP functional monomer in the two-step self-etch adhesive has shown to resist adjacent enamel at the enamel/adhesive interface against acid attack. This fact suggests that application of the coating materials can reinforce the tooth surface, 'Super Tooth', and contribute to tooth structure preservation. A recent study showed that these resin coating materials could sufficiently protect enamel against aggressive acid challenge.^[23] Soft tissue recession because of age, inappropriate toothbrush habits, periodontal disease, or surgical periodontal treatment will cause exposure of susceptible root surface and high incidence of root caries and dentin hypersensitivity. Simple single-visit methods to protect the exposed root surfaces from long-term caries attack are advantageous. Root surface coating with the dentin bonding systems is considered to be an effective measure for protection against caries, erosion, and abrasion, as it provides a strong physical barrier with the formation of Super Dentin. However, a promising approach to prevent root caries has not become available yet. From the clinical stand point, to control the biofilm adherence on the coating material is also important to reduce caries risk in the oral environment. A series of experimental coating materials with self-cleaning surface property has been developed, containing good potential to inhibit biofilm adherence.^[24] If such materials with a surface property could be combined with the current adhesive technology, the surface coating will become a promising therapy in preventive dentistry in the future.

Current challenges

Despite the promising results and concepts, several challenges still remain in adhesive dentistry. Bonding to the clinical substrate is more challenging than that in laboratory conditions as the dentin may undergo various alterations due to aging, caries or other conditions which influence its permeability and bonding potential. Bonding to enamel may still require micromechanical interlocking through an increased surface porosity by stronger acids followed by monomer diffusion compared to the naturally permeable dentin. In addition to the substrate, the most recent adhesive materials accepted as golden standards still face challenges ranging from pre-usage shelf life and usage technique sensitivity to the loss of

long-term integrity and durability of the resin. Even if dentin is protected, polymerization shrinkage of the dental composites and stress developed thereby along with other adaptation factors may deteriorate longevity due to gap or marginal disintegration. Also, the hydrophilic-hydrophobic balance of formulations is a major obstacle for the all-in-one adhesives, challenging the adhesion to both dental hard tissue and direct composite resins. Last but not least, more biocompatible and nontoxic materials which can biomineralize tissue are desired in the future to further realize the super dentin.

REFERENCES

1. Kidd EA Diagnosis of secondary caries. *J Dent Educ*, 2001; 65(10): 997–1000.
2. Kuper NK, van de Sande F, Opdam NJ, Bronkhorst EM, de Soet JJ, Cenci MS, Huysmans MC Restoration materials and secondary caries using an in vitro biofilm model. *J Dent Res*, 2015; 94(1): 62–68.
3. Nakabayashi N, Nakamura M, Yasuda N. Hybrid layer as a dentin bonding mechanism. *J Aesthet Dent*, 1991; 3: 133–8.
4. Pashley DH, Carvalho RM. Dentin permeability and dentine adhesion. *J Dent*, 1997; 25: 355–72.
5. Tsuchiya S, Nikaido T, Sonoda H, Foxton RM, Tagami J. Ultrastructure of the dentin—adhesive interface after acid base challenge. *J Adhes Dent*, 2004; 6: 183–90.
6. Toru Nikaido, Go Inoue, Tomohiro Takagaki, Kanchana Waidyasekera, Yasuhiro Iida, Mirela S. Shinohara, Alireza Sadr, Junji Tagami; New strategy to create “Super Dentin” using adhesive technology: Reinforcement of adhesive—dentin interface and protection of tooth structures; *Japanese Dental Science Review*, 2011; 47: 31–42.
7. Shinohara MS, Yamauti M, Inoue G, Nikaido T, Tagami J, Giannini M, et al. Evaluation of antibacterial and fluoride-releasing adhesive system on dentin—microtensile bond strength and acid—base challenge. *Dent Mater J*, 2006; 25: 545–52.
8. Y. Yoshida, K. Nagakane, R. Fukuda, Y. Nakayama, M. Okazaki, H. Shintani, S. Inoue, Y. Tagawa, K. Suzuki, J. De Munck, B. Van Meerbeek, Comparative study on adhesive performance of functional monomers. *J. Dent. Res*, 2004; 83: 454-458.
9. Marcelo Giannini, Patrícia Makishi, Ana Paula Almeida Ayres, Paulo Moreira Vermelho, Bruna Marin Fronza, Toru Nikaido, Junji Tagami; Self-Etch Adhesive Systems:A Literature Review; *Braz Dent J*, 2015; 26(1).

10. Kaneshiro AV, Imazato S, Ebisu S, Tanaka S, Tanaka Y, Sano H. Effects of a self-etching resin coating system to prevent demineralization of root surfaces. *Dent Mater*, 2008; 24: 1420—7.
11. Toru Nikaido, Go Inoue, Tomohiro Takagaki, Rena Takahashi, Alireza Sadr, Junji Tagami; Resin Coating Technique for Protection of Pulp and Increasing Bonding in Indirect Restoration; *Curr Oral Health Rep*, 2015; 2: 81–86.
12. Tay FR, Pashley DH, Suh BI, Carvalho RM, Itthagarun A. Singlestep adhesives are permeable membranes. *J Dent*, 2002; 30: 371—82.
13. Hiraishi N, Kitasako Y, Nikaido T, Foxton RM, Tagami J, Nomura S. Detection of acidic diffusion through bovine dentine after adhesive application. *Int Endod J*, 2004; 37: 455—62.
14. Tay FR, King NM, Chan KM, Pashley DH. How can nanoleakage occur in self-etching adhesive systems that demineralize and infiltrate simultaneously? *J Adhes Dent*, 2002; 4: 255—69.
15. Nikaido T, Nishimura M, Iida Y, Inoue G, Tagami J. SEM observation of acid—base resistant zone in all-in-one adhesive systems. *Adhes Dent*, 2007; 25: 197—203. (in Japanese with English abstract).
16. Takagaki T, Nikaido T, Tsuchiya S, Ikeda M, Foxton RM, Tagami J. Effect of hybridization on bond strength and adhesive interface after acid—base challenge using 4-META/MMA-TBB resin. *Dent Mater J*, 2009; 28: 185—93.
17. Nakabayashi N, Takeyama M, Kojima K, Masuhara E. Studies on dental self-curing resins. Adhesion of 4-META/MMA-TBB resin to pretreated dentine. *J Dent Mater*, 1982; 1: 74—7.
18. Kosaka S et al. Effect of resin coating as a means of preventing marginal leakage beneath full cast crowns. *Dent Mater J*, 2005; 24(1): 117–22.
19. Nikaido T et al. The resin-coating technique. Effect of a single-step bonding system on dentin bond strengths. *J Adhes Dent*, 2003; 5(4): 293–300.
20. Takahashi R et al. Thin resin coating by dual-application of all-in-one adhesives improves dentin bond strength of resin cements for indirect restorations. *Dent Mater J*, 2010; 29(5): 615–22.
21. Horowitz HS, Heifetz SB, Poulsen S. Retention and effectiveness of a single application of an adhesive sealant in preventing occlusal caries: final report after five years of a study in Kalispell, Montana. *J Am Dent Assoc*, 1977; 95(6): 1133–2119.

22. Ariyoshi Met al. Microtensile bond strengths of composite cores to pulpal floor dentin with resin coating. *Dent Mater J.*, 2008; 27(3): 400–7.
23. Heijnsbroek M, Paraskevas S, van der Weijden GA. Fluoride interventions for root caries: a review. *Oral Health Prev Dent*, 2007; 5(2): 145–52.
24. Gando I et al. Resistance of dentin coating materials against abrasion by toothbrush. *Dent Mater J.*, 2013; 32(1): 68–74.