



THE EFFECT OF DIFFERENT ADHESIVES USED AS THE IMMEDIATE
DENTIN SEALING ON THE ADHESION OF THE RESIN CEMENT TO DENTIN



NONGLAK PHEERARANGSIKUL

A Thesis Submitted to the Graduate School of Naresuan University
in Partial Fulfillment of the Requirements
for the Master of Science in (Master of Sciences in Dentistry (Operative Dentistry) -
Type A 2)
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By NONGLAK PHEERARANGSIKUL

has been approved by the Graduate School as partial fulfillment of the requirements
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Type A 2 of Naresuan University

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Title

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Keywords

Immediate dentin sealing, Dental adhesive, Functional
monomers, Shear bond strength, Resin cement

ABSTRACT

Immediate dentin sealing (IDS) is the process of applying dental adhesives on the fresh-cut dentin of indirect tooth preparation. The IDS could be either etch-and-rinse or self-etch adhesive systems. After IDS, the adhesive for the resin cement is applied on top of the polymerized IDS. Then the restoration is cemented. The bondability at the interfaces between IDS and the resin cement adhesive is controversial because of the different compositions between them.

Objective: To evaluate the shear bond strength of the resin cement when applied along with the immediate dentin sealings, which have different dental adhesives.

Methods: Sound human premolar teeth extracted for orthodontic treatment were selected for this study. The coronal

half of the tooth was removed to receive the dentin surface. These teeth were divided into 13 groups (n=10) according to the dental adhesives (IDS) and the dental adhesives of resin cement. There were five baseline groups (no IDS); PV5, OXTR/NX3, SCB, SBU/RU(TE), and SBU/RU(SE), four groups of similar compositions of the dental adhesives; CSE-PV5, OXTR-OXTR/NX3, SBU-SBU/RU(TE), and SBU-SBU/RU(SE), and four groups of different dental adhesives; OXTR-PV5, CSE-OXTR/NX3, OXTR-SCB, and CSE-SCB. After the IDS was performed and polymerized, the surfaces were wiped with 70% ethyl alcohol and polished with pumice. A resin composite rod treated surface with sandblasting was bonded on the dentin surface with resin cement as designed. The specimens were stored in distilled water at 37 °C for 24 hours, followed by thermocycling 5,000 cycles. The specimens were encountered the shear bond test with a universal testing machine and statistically analyzed by One-Way ANOVA. A scanning electron microscope (SEM) was also used to analyze the fracture characteristics of specimens; adhesive failure and cohesive failure of each substrate.

Results: The RelyXTM UltimateTM, which applied along with the Single Bond Universal Adhesive, with either etch-and-rinse or self-etch system, had the highest shear bond strength

with no statistical difference in their shear bond strength between with and without the IDS. The NX3 NexusTM with the GPDM functional monomer, the shear bond strength significantly increased when applied the IDS with the similar-composition with the resin cement adhesive. The different-composition IDS and the resin cement adhesive could not increase the shear bond strength.

Conclusion: Similar-composition of dental adhesives between the IDS and the dental adhesives of resin cement significantly provided higher shear bond strength when compared with different-compositions. When applying the Single Bond Universal Adhesive along with RelyXTM UltimateTM resin cement with or without the IDS provided the highest shear bond strength with no difference between them.

ACKNOWLEDGEMENTS

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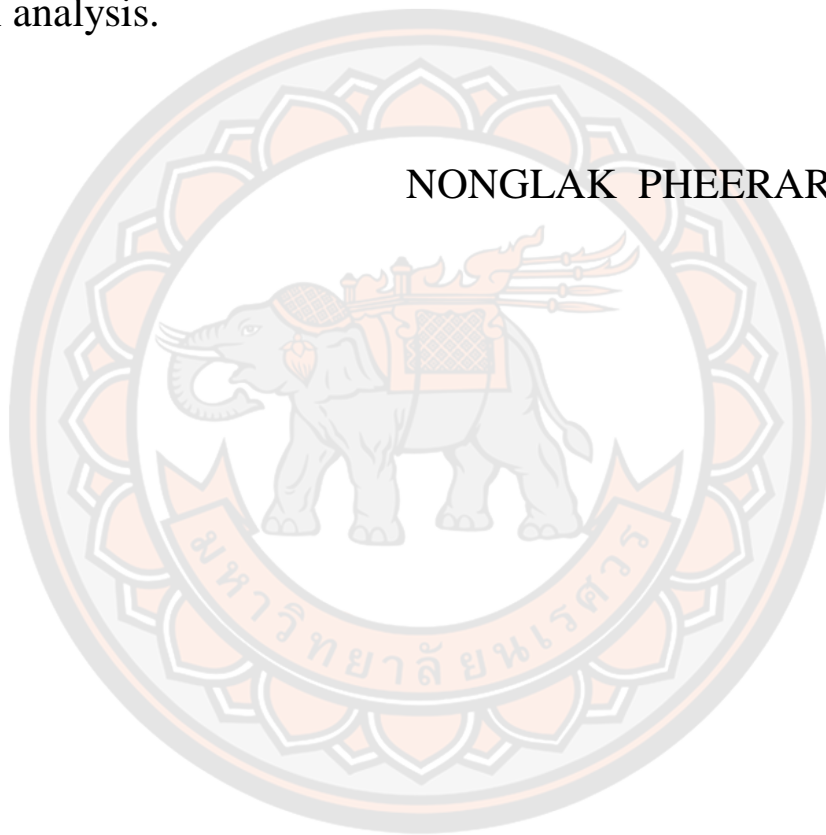
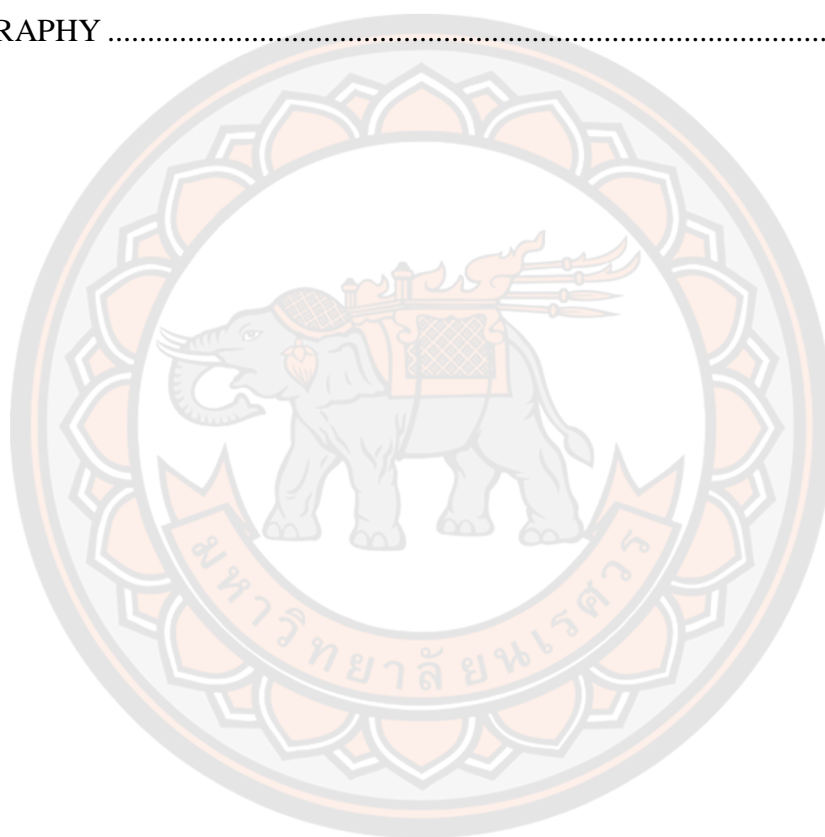


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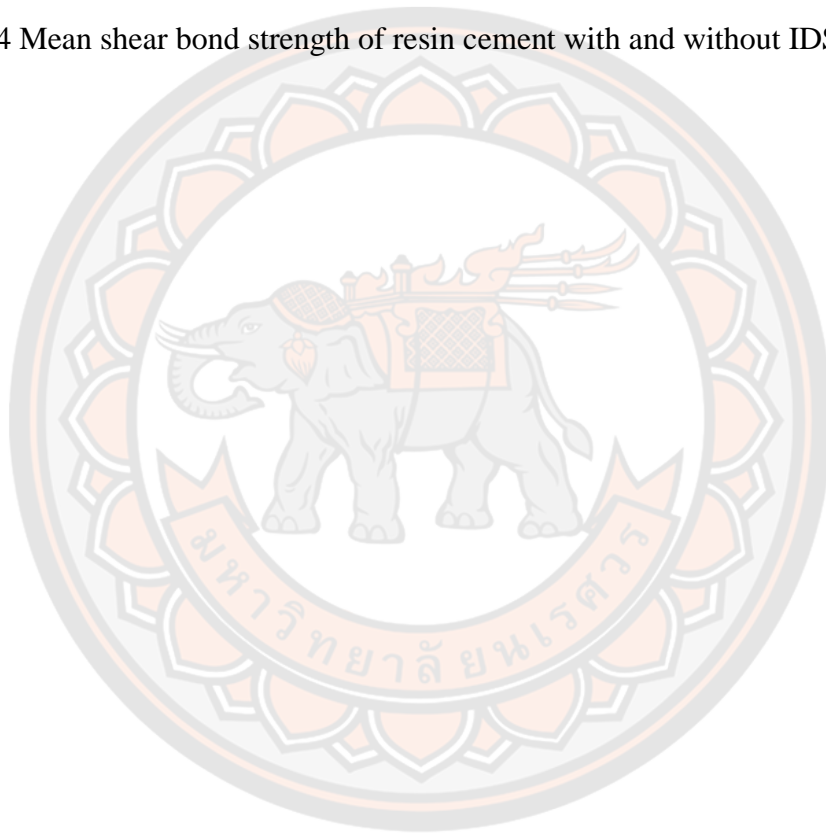
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Chapter 1

Introduction

1.1 Background

The purposes of dental restorations are to repair and to reconstruct the functions, morphology and integrity of destroying the tooth structure. It is largely classified into direct and indirect procedures which are mainly considered from the amount of the destructed tooth. The direct technique can preserve more natural tooth structure, but it is difficult to achieve a proper contour or occlusion when processes intra-orally.

Regarding the indirect technique, it is the common method when a large amount of tooth is destructed. Restorations are commonly fabricated extra-orally and then cemented intra-orally. A cementation is a vital procedure for the longevity of the restorations. The conventional luting cements are non-bondable to either tooth structure or restoration substrates. They fill spaces and retain the restorations by friction. An innovation of an adhesive resin cement due to the application of an adhesive system along with the resin-based cement can introduce the bondable cementation on both the tooth structure and the restorative materials under proper surface modifications.

There are numerous resin cement products in the market. They have different chemical compositions that influence adhesion ability. According to the clinical application technique, there are mainly three systems; etch-and-rinse, self-etch, and self-adhesive resin cement. The etch-and-rinse system has a separated phosphoric acid for preparing the tooth abutment. Either primer or adhesives of the self-etch systems are acidity from acidic functional monomers for tooth preparation. The resin cement of the self-adhesive system is acidity due to the acidic functional monomers mixed into this single component.

Immediate dentin sealing (IDS) is the process to apply the dental adhesives on the exposed dentin during tooth preparation for indirect restorations to prevent the penetration of bacteria and fluid into the dentinal tubules during using the temporary restorations (1, 2). The dental adhesive for IDS can be either an etch-and-rinse system or self-etch system (3). The IDS is unavoidable to contact the resin cement in the process of permanent restoration cementation.

The compatibility of IDS and adhesive system of the resin cement can create the complete bond of the resin cement. When using either the self-etch or self-adhesive systems, the IDS and the resin cement with different dental adhesives might be no effect on the bond efficiency.

1.2 Purposes of the Study

To evaluate the shear bond strength of the resin cement when applied along with the immediate dentin sealings, which have different dental adhesives.

1.3 Research Significance

The information from this study can use as the guideline for selecting the dental adhesives when performing the immediate dentin sealings along with the resin cement for the indirect restorative treatment.

1.4 Research Scope

An experimental research

1.5 Basic Assumption

The effect of different dental adhesives in the immediate dentin sealing and resin cement has no effect on the shear bond strength of resin cement.

1.6 Key Words

Immediate dentin sealing, Dental adhesive, Functional monomers, Shear bond strength, Resin cement

1.7 Research Hypothesis

The different dental adhesives in the immediate dentine sealings and resin cements have no effect on the shear bond strength of the cemented restorations.

Chapter 2

Review Literature

The purposes of dental restorative treatment are restoring both functions and aesthetics to the masticatory systems. Many restorative materials are discovered to imitate the natural tooth structures. The natural tooth structures are complicated. They are composed of the soft pulpal tissue circumscribed with the flexible dentin layer and the outermost brittle enamel. However, none can provide the satisfying biological, mechanical, and physical properties compared with the natural structure.

The conservative dentistry has been proposed as the natural tooth structures are the most durable material. An adhesive system plays a crucial role to preserve the tooth structure. Plenty of modern restorative materials are bondable when used along with the adhesive system.

Dental restorative treatment can be divided into the direct and indirect techniques. For the direct technique, the low viscous bonding agent is the intermediate substance to bond the restorative materials to the tooth structure. It is also applied to the same purpose in the indirect technique which required additional luting cement or adhesive cement to retain the restorations.

Dental Adhesives

Etchant, primer, and dentin bonding agents are basic components of dental adhesive systems. These adhesives are used to create the adhesion between restorative materials; ceramics, metals, resin composite, and tooth structure.

Dental adhesives are the low viscous resin which can penetrate into the deep cleavage area resulting in the micromechanical retention after polymerization. The chemical compositions of dental adhesive contain both hydrophilic and hydrophobic monomers, including polymerization initiators, stabilizers, solvents, and an inorganic filler.

The dentin bonding agent simply applies to the dentin. The adhesives for the immediate dentin sealing can be either an etch-and-rinse system or a self-etch system. For the etch-and-rinse system, the characteristic that occurs in dentin after etchant exposure is the demineralization of hydroxyapatite at the inter-tubular dentin and the peritubular dentin for 5-8 μm in depth resulting in the collagen fibril exposure (4). A primer facilitates the penetration of the bonding agent by improving the wettability, re-expanding the collagen network, and removing excess water (5). The dentin bonding agent has the resin monomers that infiltrates into the inter-collagen fiber spaces and the dentinal tubules forming the hybrid layer and the resin tags after polymerization (6). A hybrid layer is a layer consisting of a blend of collagen fibers and resin. This is a layer of resin that passes into some of the demineralized dentin and the irregular part of the dentin under collagen meshwork.

Regarding the resin monomers in the dental adhesives, there are several monomers intermingled as the compositions. The bisphenol glycidyl methacrylate (Bis-GMA) and the hydroxyethyl methacrylate (HEMA) are the most popular monomers in the dental adhesives. The HEMA and the triethylene glycol dimethacrylate (TEGDMA) are hydrophilic monomers while the Bis-GMA and the

urethane dimethacrylate (UDMA) have more hydrophobic properties which are normally added into the dentin bonding agent.

Bis-GMA is a large monomer molecule. It is added into the dental adhesives for improving the properties. Bis-GMA is hydrophobic monomer with strong intermolecular hydrogen interactions (7). The polymerized Bis-GMA absorbs water around 3%. The mixed HEMA - Bis-GMA adhesive increases the wettability, diffusion, and penetration of the adhesive into the dentin (8).

UDMA is a smaller molecular monomer compared with Bis-GMA. UDMA has a lower viscosity and higher flexibility than Bis-GMA. The high percentages of UDMA in dental adhesives increase the viscosity and bond strength of the dental adhesive with no effect on the degree of conversion. This result is caused by UDMA has a very flexible backbone together with a weak hydrogen bond of the urethane groups. The UDMA polymers have higher degree of conversion compared with Bis-GMA. Therefore, UDMA provides better mechanical strength (7).

HEMA is the small monomer molecule. Uncured HEMA dissolves in the solvents such as water, ethanol, and/or acetone. One of the important features of HEMA is hydrophilic property, so HEMA can properly function within the moist dentin as the adhesion-promoting monomer. However, the hydrophilic property of HEMA makes the uncured adhesives absorb water, which deteriorates the polymerized adhesives.

TEGDMA is a small monomer molecule. It does not have a strong intermolecular bond, so the TEGDMA is highly flexible and low viscosity. It has three times a higher degree of conversion than the Bis-GMA (9).

For the self-etch adhesive system, the acidic monomers modify the smear layer and smear plug instead of removal. They demineralize and penetrate into these layers simultaneously. This system produces the hybrid layer 0.5-1.2 μm in thickness and short narrow resin tags. The acidity of the acidic monomers is lower than that of the phosphoric acid in the etch-and-rinse system and that makes the self-etch system has less ability to demineralize dentin (10).

Comparison between the one-step and two-step self-etch adhesives, the former has higher concentration of acidic monomer for efficient demineralization, which comes along with the insufficiency of the hydrophobic adhesive layer. It increases the passing rate of water from the dentinal tubules and causes the drops of water at the adhesive-interface area (11).

Universal adhesive or multi-mode adhesive can use in different modes such as etch-and-rinse, self-etch, or combination with selective etch. When considering the modes of application, they revealed that the universal adhesive with selective-etch preforms a lower percentage of discoloration the enamel margin (12). Universal adhesive combined with a selective-etch improves bond durability on enamel (13-15).

Single Bond Universal Adhesive (3M ESPE, St Paul, MN, USA) is the first universal adhesive launched in the market. The 10-methacryloxydecyl dihydrogen phosphate (10-MDP) is a functional monomer that many companies added to universal adhesives. In addition, universal adhesive contained biphenyl dimethacrylate (BPDMA), dipentaerythritol pentaacrylate phosphoric acid ester (PENTA), and polyalkenoic acid copolymer (methacrylate modified polyalkenoic acid or Vitrebond Copolymer (VBCP)). When a bond reaction occurred, the VBCP in a universal adhesive creates a chemical bond with hydroxyapatite immediately with the

same mechanism as the VBCP in glass ionomer materials. The VBCP has ionic bonds to tooth substrate, which promotes strong adhesion to tooth structures but less than micromechanical retention. This structure is resistant to hydrolytic degradation (10, 16). Owing to combining elements among hydrophobic (decandiol dimetacrylate/D3MA and Bis-GMA), and hydrophilic (hydroxyethyl methacrylate/HEMA) monomers in the matrices, this dental adhesive produces a very durable and strong bond between hydrophilic tooth substrate and hydrophobic resin-based restoration (8).

The Single Bond Universal Adhesive is the silane containing adhesive that facilitated the bondability between the new and the aged resin composites (17). After silane is hydrolyzed to silanol, the silanol group molecules function as an intermediate reagent by forming a polysiloxane network to bond to both the resin matrix and glass filler particles of either new or aged resin composite. When compared longevity between Single Bond Universal Adhesive (MDP-VBCP) and Adper Single Bond 2 (3M ESPE, St Paul, MN, USA) by evaluating bond strength, the study revealed that the MDP-VBCP improved bonding ability (18).

Functional Monomers

Functional monomers are the most important composition in the self-etch adhesive system. They determine the properties of the adhesive agents. The functional monomer molecule is composed of three domains in the structure; polymerizable groups, spacer, and acidic functional groups. The polymerizable methacrylate groups have the hydrophobic property. They are able to co-polymerize with other monomers for creating the resin matrix polymers. The spacer is a linkage between the acidic functional group and the polymerizable groups. This domain composes of many chain groups, such as alkyl, ester, amide, or aromatic groups. The polarity of the spacer determines the solubility of the adhesive. The size of spacer indicates the viscosity and the infiltrating capability. In addition, the spacer has an influence on the flexibility of the monomers. The acidic functional group mainly determines the hydrophilic properties of the monomer. This group has several functional groups such as phosphate, phosphonate, sulfonic and carboxyl groups. The functions of this domain are directly associated with the wettability and the demineralization ability of the functional monomers (Figure 1) (19).

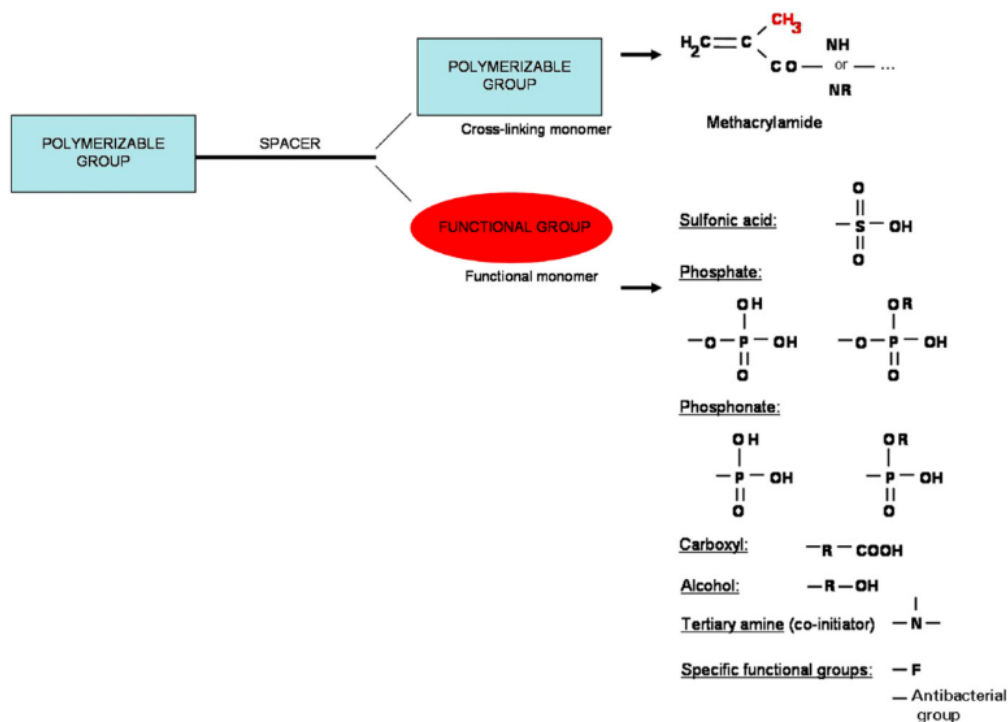


Figure 1 The structures of the acidic functional monomers containing 3 domains; polymerizable group, spacer, and acidic functional domain. There are several acidic functional domains which have different molecular structures such as sulphonic group, phosphate group, phosphonate group, or carboxylic group (19)

There are several acidic functional monomers in dentistry such as phosphate, phosphonate, sulfonic, and carboxyl groups. The carboxyl and phosphate groups are possibly hydrolyzed in the water while the sulfonic groups are more hardly dissolved in water (20). Regarding the demineralizing ability, the sulfonic groups have the highest efficiency followed by the phosphonic (H_3PO_3), phosphoric (H_3PO_4), and carboxylic groups (21).

There are two groups of phosphorus acidic monomers as phosphonate ($\text{R}-\text{O}_3\text{P}^-$) and phosphate (PO_4^{3-}). The phosphorus-carbon bond in the phosphonate has higher enzymatic-degradation resistance compared with the phosphorus-oxygen bond of the phosphate group (21). However, the phosphonate group has more free electrons and higher acidity than the phosphate group (22). There are several functional monomers with the phosphate-based (PO_4^{3-}) functional molecules as 2-methacryloyloxyethyl dihydrogen phosphate (MEP, $\text{C}_6\text{H}_{11}\text{O}_6\text{P}$), Glycerophosphate dimethacrylate (GPDM), 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP, $\text{C}_{14}\text{H}_{27}\text{O}_6\text{P}$), and 12-methacryloyloxy-dodecyl-dihydrogen phosphate (12-MDDP) (19).

A Phenyl-P is the pioneer acidic monomer in the phenyl group. This functional monomer can demineralize the hydroxyapatite of dentin to get the collagen exposure approximately $1\ \mu\text{m}$ in-depth and form the superficial hybrid layer (23). It has a small chemical bond to the tooth structure. Phenyl-P induces the deposit of dicalcium phosphate dihydrate (DCPD; $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) on the decalcified apatite around collagen fibril. This monomer-collagen complex is less stable than the original

apatite crystal (24, 25). For this reason, this monomer is not popular in the dental adhesive.

A Glycerophosphate dimethacrylate (GPDM) is a phosphate acidic monomer with one phosphate acidic functional group and two polymerizable methacrylate groups. This functional monomer is a small molecule with more hydrophilicity than the 10-MDP. The GPDM is similar to the HEMA and that makes it easily penetrate into the demineralized dentin. From the transmission electron microscopy (TEM), the GPDM creates a thick hybrid layer, and it has no nano-layering appearance (Figure 2 and 3) (26).

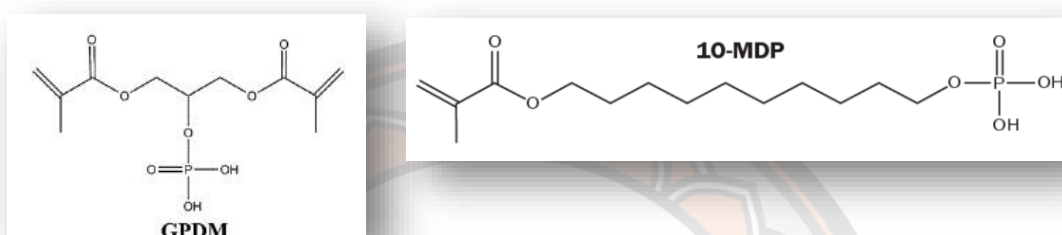


Figure 2 The chemical structure of GPDM and 10-MDP

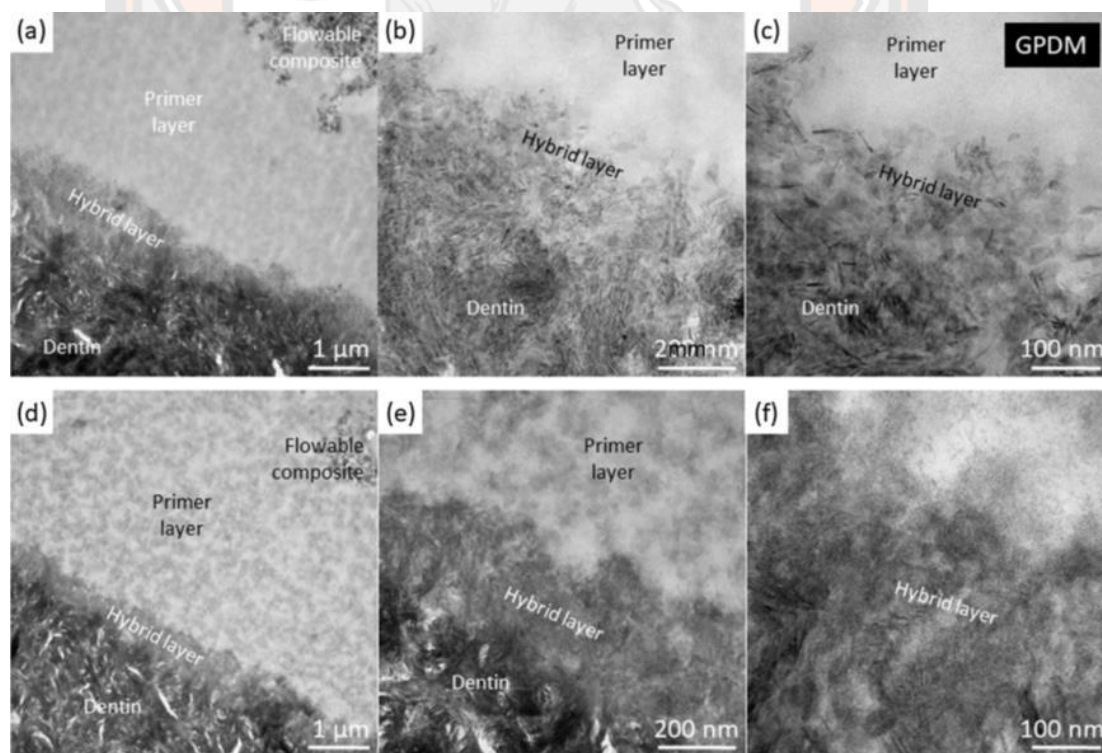


Figure 3 TEM photomicrograph of 15% by weight of the GPDM primer applied on dentin (a-f), with no co-localization (a-c), and with co-localization (d-f) of collagen (26).

A 2-methacryloyloxyethyl dihydrogen phosphate (MEP) is a phosphate functional monomer that is unstable in water. When the MEP monomer dissolve in water, it has strong acidic property causing demineralization of the enamel and dentin (27). MEP decalcified more than adhered to dentin surface might be correlated with non-stable of ionic interaction between this monomer and hydroxyapatite. Since MEP had lower molecular weight, it could penetrate to the deep part of dentin. After rinsing off with the distilled water, the dentinal tubule exposed with no resin tag or MEP monomer covering on the dentin, while the monomer of other dental adhesives still remaining on the dentin surface (28).

Among the phosphate functional monomers, a 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) is the most popular monomer. The 10-MDP has the chemical interaction with the hydroxyapatite along with the demineralized tooth structure forming the MDP-Ca salt complex. This monomer has strong ionic bonds to the tooth structure. In the TEM photographs, the MDP-Ca complex presents nano-layering architecture (25). This layer consists of long linear alkyl chains and phosphoric acid ester groups. The nanolayers parallelly arrange in 12-15 layers (29). (Figure 4 and 5). This organization results in a very intrepid chemical bond to the hydroxyapatite (30). This complex structure is stable and durable, so it has a higher withstanding to hydrolytic degradation compared to other functional monomers (30). The 10-MDP and 12-MDDP (12-methacryloyloxy-dodecyl-dihydrogen phosphate) have 10 and 12 carbon chain spacers, respectively. They are more hydrophobic than other short-chain phosphate-based acidic monomers, so the 10-MDP- and 12-MDDP-based dental adhesives are more stable than others. But these two monomers have no statistical difference in their calcium salt formation on dentin (Figure 6) (28).

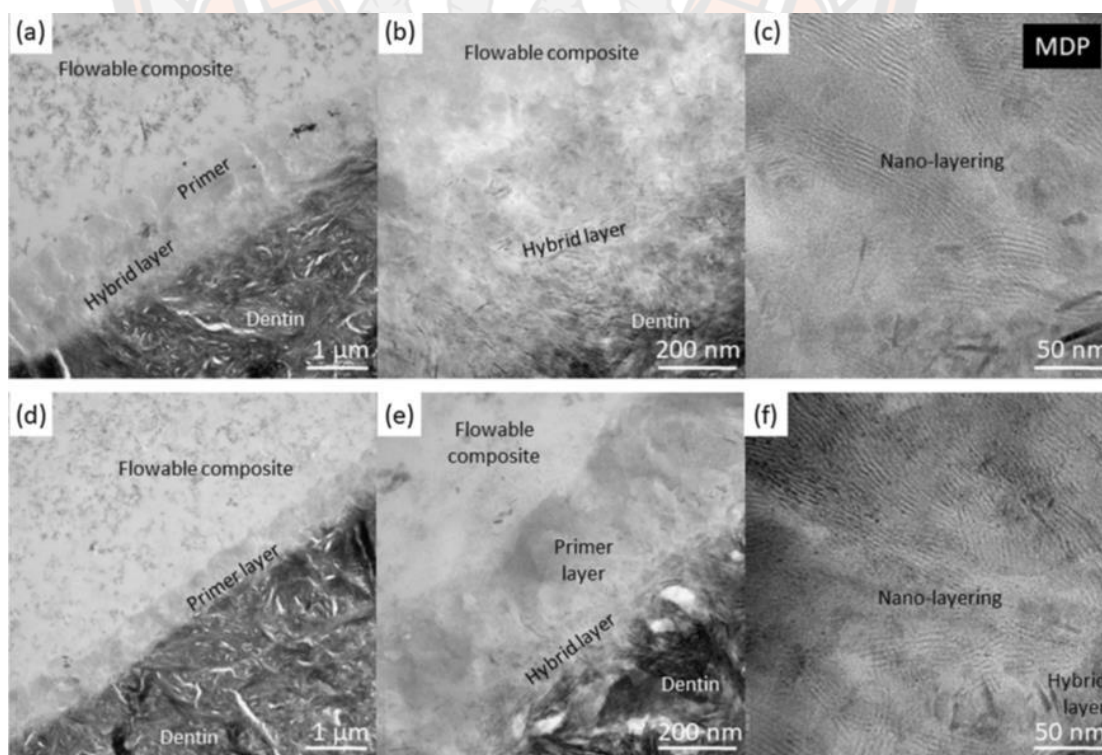


Figure 4 TEM photomicrograph of 15% by weight of the 10-MDP primer applied on dentin (a-f), with no co-localization (a-c), and with co-localization (d-f) of collagen (26).

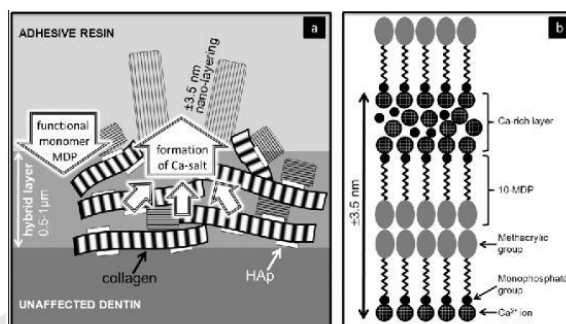


Figure 5 The structure of the nano-layering appearance: (a) MDP-Ca salt complex formation in the hybrid layer, (b) nano-structural arrangement of nano-layering (31).

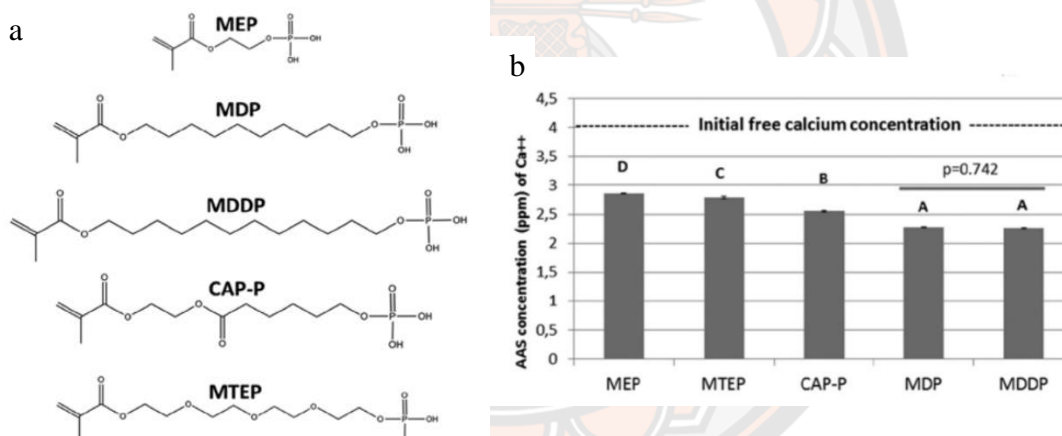


Figure 6 The phosphate-base functional monomers,

(a) the chemical structure of the phosphate-base functional monomers, MEP = 2-methacryloyloxy-ethyl-dihydrogen phosphate(2-MEP), MDP = 10-methacryloyloxy-decyl-dihydrogen phosphate (10-MDP), MDDP = 12-methacryloyloxy-dodecyl-dihydrogen phosphate (12-MDDP), CAP-P = methacryloyloxy-caprolactone dihydrogen phosphate, MTEP = methacryloyloxy-tetraethylene-glycol-dihydrogen phosphate

(b) Atomic absorption spectroscopy (AAS) shows the concentration of free remaining calcium ions. The concentration of free calcium ions conversely related to the number of carbon atoms in the spacer of the acidic functional monomers, since the acidic functional monomers with a large number of carbon atoms has a higher ability to bind to the calcium ions (28).

For the carboxyl functional monomers, 4-methacryloxyethyl trimellitic acid (4-META) is the most popular one. Its carboxylic groups attach with the aromatic groups. The aromatic groups have the hydrophobic property which has the ability to buffer the acidity and to reduce the hydrophilicity of the carboxylic groups. This acidic monomers bond to calcium in hydroxyapatite and form the Ca-4MET salt (32). The formation of a submicron hybrid layer with apatite crystal around collagen fibril results in a more durable bond compared to the Phenyl-P monomer adhesives (24). However, the chemical bond of 4-MET is weaker compared to 10-MDP (30). The 4MET is the hydrolyzed form of the 4-META (Figure 7). When it is used with the methyl methacrylate (MMA), they form the 4-META/MMA-TBB (tri-n-butyl borane) molecule (30).

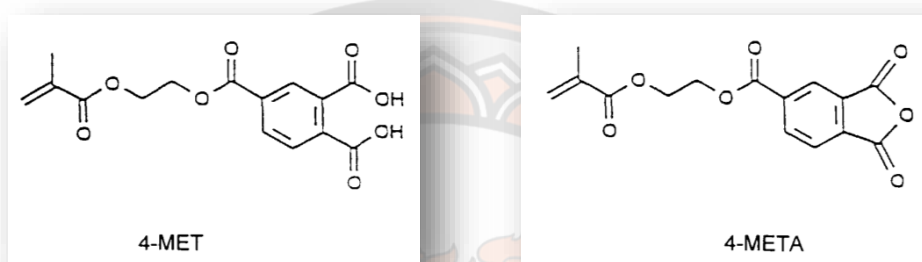


Figure 7 The chemical structure of 4-MET and 4-META

A 4-acryloyloxyethyl trimellitate anhydride (4-AETA) monomer is different from 4-META. The 4-AETA contains an acrylic polymerizable group instead of a methacrylate group. This acrylic group allows the dental adhesive to be more polymerized than the methacrylate group. Previous studies found that 6-10 carbon atoms in a molecule showed a stable molecular layer on the adherent surfaces (33). The bond strength of 4-AETA clearly decreased when undergone the thermocycling 10,000–20,000 cycles (33).

A methacryloyloxydodecylpyridinium bromide (MPDB) has a bactericidal effect from both before and after polymerization. It has a positive charge binding to the bacterial cell membrane, causing the direct destruction of microorganisms. Quaternary ammonium monomers in MDPB are the main composition to destroy *S. mutans* (34) in both planktonic and biofilm within 60 seconds. The low concentration of MDPB suppresses the lactate dehydrogenase activity. When MDPB added into the dental adhesive, there has no effect on the bond strength of the bonding agent (35).

The Adhesion-Decalcification concept (AD-concept) is an ionic bond that formed between an acidic molecule and hydroxyapatite. In the first bonding phase, hydroxyapatite is dissolved and releases phosphate and hydroxide in its own solution. The functional monomer molecule bonded property with hydroxyapatite depends on the stability of bonding with calcium. The interactions of each functional monomer can explain by AD-concept (Figure 8 and 9).

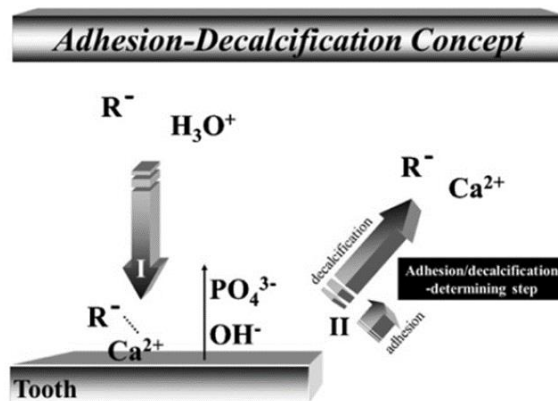


Figure 8 The Adhesion-Decalcification concept (AD-concept) explains the ionic interaction between the acidic functional monomers and hydroxyapatite. There are 2 possibilities of this interaction: (1) Ca-monomer salt formation occurred from the ionic bond between acidic monomer and calcium ions of hydroxyapatite. When this Ca-monomer salt is stable, the hydrolytic degradation hardly occurred. (2) When the Ca-monomer salt is unstable, the calcium and phosphate dissolve from the tooth surface resulting in decalcification (36).

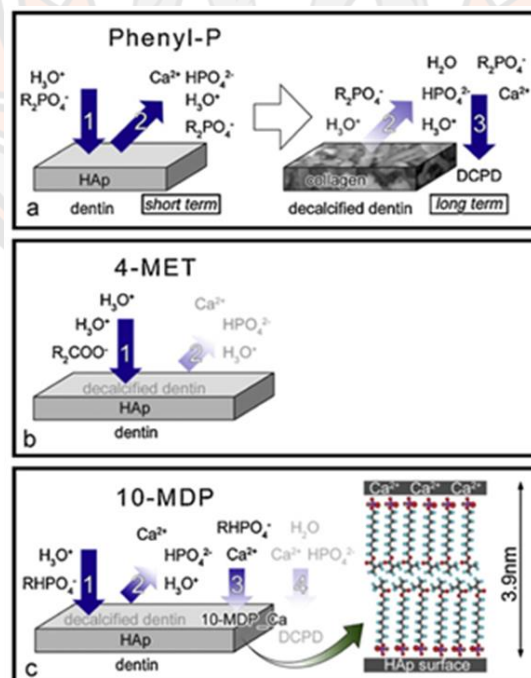


Figure 9 Molecular interactions of three functional monomers at the bio-material-hard tissue interface (36).

- (a) The functional group of Phenyl-P (hydrogen phosphate (HPO_4^{2-})) binds to the calcium ions, which are dissolved from the hydroxyapatite. The Phenyl-P_calcium compounds are easily dissolved in the solution. Together with abundant phosphate (PO_4^{3-}) and hydroxide (OH^-) ions from the dissolved hydroxyapatite, there is rapid deposition of dicalcium phosphate dihydrate (DCPD; $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). However, DCPD does not protect collagen networks better than primary apatite crystals.
- (b) The functional group of 4-MET (hydrogen phosphate (HPO_4^{2-})) binds to the calcium ions with weak chemical bond. The 4-MET_calcium compounds are hardly dissolved compared to the Phenyl-P_calcium compounds. When the amount of calcium, phosphate, and hydroxide ions is large enough, the DCPD is formed. This situation rarely occurred within the observation time.
- (c) The functional group of 10-MDP (hydrogen phosphate (HPO_4^{2-})) binds to the calcium ions with the stronger chemical bond and durable due to the self-assembled nanolayering structure. The nanolayering structure consists of two methacrylate groups join to each other. The phosphate group binds to the calcium ion of the hydroxyapatite. The initial formation of the MDP-calcium complex functions as a nucleus. This process continuously occurs to be the MDP-calcium crystals on the hydroxyapatite surface. This structure is called self-assembled nanolayering. This MDP-Ca salt is the most stable chemical compound when compare with others. This structure might be able to increase the bond strength. Even the phosphate (PO_4^{3-}) and hydroxide (OH^-) ions dissolved from the hydroxyapatite are not high enough to form the DCPD.

Resin Cement

Resin cement is an adhesive cement. It is able to bond to several substrates when used along with the appropriate primers and the adhesive systems. When compared with the conventional luting cement, the resin cement has many preferable features such as high bond strength, compressive strength, tensile strength, flexural strength, modulus of elasticity, and low solubility (37). However, the resin cement has technique sensitivity and difficulty in cleaning. This cement is the recommended material in esthetic restorations. The composition of the resin cement is similar to the resin composite. Resin cement can be classified according to the adhesive scheme to be the etch-and-rinse, self-etch, and self-adhesive resin cement.

The etch-and-rinse resin cement needs the preparation of the tooth substrate with 30-40% phosphoric acid. The smear layer, smear plug, and hydroxyapatite are removed leading to the exposure of the dentinal tubules and the collagen. The characteristic that occurs in the dentin after etchant exposure is the demineralization of hydroxyapatite at the inter-tubular dentin and the peritubular dentin for 5-8 μm in-depth resulting in collagen exposure (4). The dentin bonding agent has the resin monomers that infiltrate into the inter-collagen spaces and the dentinal tubules forming the hybrid layer and the resin tags after polymerization (6).

Etch-and-rinse resin cement and self-etch resin cement have no significant differences in bond strength in the pull-out glass fiber post-test (38). Nevertheless, Torres et al. found that the etch-and-rinse resin cement has significantly higher bond strength when compared with self-etch resin cement and self-adhesive resin cement

(39). Etch-and-rinse resin cement has lower microleakage than self-etch resin cement in the enamel area (40). The etch-and-rinse system has technique sensitivity due to the many steps in clinical application. This can make a risk of contamination during operation. The examples of the etch-and-rinse resin cement are RelyX™ ARC Adhesive Resin Cement (3M ESPE), Variolink® II (Ivoclarvivadent Inc.), Choice 2 (BISCO, Inc.), and Calibra veneer (Dentsply).

The tooth surfaces are prepared by the self-etching primer in self-etch resin cement followed by whether bonding agent and resin cement. The self-etching system is more friendly to be used compared with the etch-and-rinse system. The bond strength and the bond durability of the two-step self-etch system are more satisfying than the one-step system when observed in water for 90 days (41). The one-step self-etch system has more hydrophilic properties, so it uptakes water and forms hydrogen bond and polar interaction, which affects its bond durability (42). The two-step self-etch system has obviously hydrophobic properties with less nanoleakage (43).

The self-adhesive resin cement is developed to simplify the clinical procedure by using as the conventional luting cement. The functional monomers also are active compositions in both the self-etch system and the self-adhesive system. The self-adhesive resin cement is bondable to tooth abutments and restorations itself. It does not need any priming agents prior used. The self-adhesive resin cement, RelyX™ Unicem (3M ESPE, St Paul, MN, USA), had no difference in marginal leakage compared to the PAVAVIA™ V5 (44-46).

Immediate Dentin Sealing

An immediate dentin sealing is a process to apply the dentin bonding agent to the fresh-cut abutment before taking the impression or placing the temporary restorations. The principle of this technique is to create an interphase or hybrid layer including resin tags to protect dentin (47). For the immediate dentin sealing adhesive, it can use along with either conventional luting cement or adhesive resin cement (48).

The immediate dentin sealing technique can increase the bond strength of the dental restorations (49). After freshly cut of the dentin, the dentin bonding agent is applied to protect the dentin from contamination, to seal the dentinal tubules, to maintain the geometry of the collagen fibers, and to decrease gaps between the dentin-adhesive interface (50). The dentin bonding agent is recommended to apply after the tooth freshly prepared before allowing the dentin exposed to either impression materials or temporary materials. The residues of these materials able to interfere with the bond efficacy of the resin cement (51). During using the temporary restorations, the hybrid layer and resin tags gradually mature, resulting in the stability of collagen fibers in the hybrid layer. Without the immediate dentin sealing, the pressure from the placement of the permanent restorations activates the dentinal fluid outflow. This phenomenon dilutes the dental adhesive and blocks the penetration of the resin cement. The pressure from the insertion of the restoration can also collapse the unpolymerized resin-collagen complex, (52) resulting in a decrease in the bond strength of the resin cement.

Regarding the immediate dentin sealing procedure, it is performed on the dentin only. After tooth preparation, the dentin exposed area need to be identified particularly in the partial coverage preparations. The dentin identification can perform by applying the etchant for only 2-3 seconds followed by rinsing and drying. The

enamel shows the frothy-chalky characteristics while the dentin has a glossy appearance. The immediate dentin sealing is not performed on the enamel since it makes less space for the restoration resulting in more stress loading on the restorations (3).

The thickness of the immediately applied dentin bonding agent depends on the tooth preparation topography and the type of dentin bonding agent. In smooth or convex areas, the thickness of dentin bonding agent is around 60-80 μm and 200-300 μm in concave areas.

After polymerization of the immediate dentin sealing, glycerine jelly is applied on the bonding agent as the air blocking agent to limit the oxygen inhibiting layer and followed by the additional polymerization for 10 seconds (53).

Oxygen Inhibiting Layer

On the surface of the dentin bonding agent commonly has the oxygen inhibiting layer. This layer looks like jelly resulting from the unreacted monomers in the polymerization procedure when in contact with oxygen in the atmosphere (Figure 10). The thickness of the oxygen inhibition layer is approximately 40 μm . These non-polymerized monomers can inhibit the polymerization reaction of the impression materials (51).

The most popular impression materials in clinical usage are elastomeric impression materials; polyvinyl siloxane and polyether. The oxygen inhibiting layer from several resin-based materials; such as flowable or conventional resin composites and core-build up materials have an influence on the degree of polymerization on the surface of the polyvinyl siloxane and the polyether while the former gets more disadvantages (54) When applying the immediate dentin sealing adhesive, the procedures for reducing and getting rid of the oxygen inhibiting layer need to be performed such as applying an air blocking agent, polishing with pumice, or rubbing with 70% ethanol before taking the impression (53).

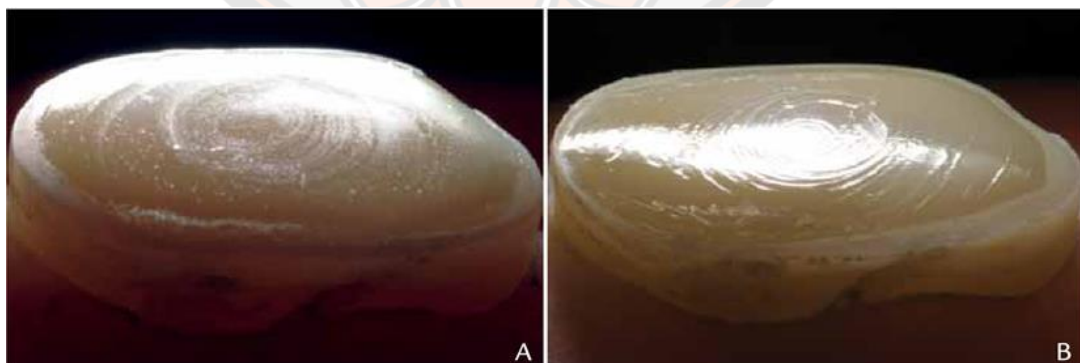


Figure 10 Specimens with oxygen inhibition layer after applying the immediate dentin sealing adhesives; Optibond FL (A) and Clearfil SE Bond (B) (51)

Adhesion between the immediate dentin sealing and the dental adhesive reagents of resin cement

After light curing of the dental adhesives, the degree of conversion may not immediately be completed. The degree of conversion has a fairly wide range according to individual materials and polymerization conditions. Generally, there is a 55-79% degree of conversion of adhesives in either the three-step etch-and-rinse and two-step self-etch adhesives after light-cured immediately (55-57). The degree of conversion of CLEARFIL™ SE Bond adhesive is 74.1 ± 1.4 when polymerized with quartz tungsten halogen (QTH), 65.5 ± 0.4 with Radii Cal LED, and 64.8 ± 0.4 with Bluephase LED. In the three-step etch and rinse and two-step self-etch adhesives, the degree of conversion with the quartz tungsten halogen (QTH) is significantly higher than light-emitting diode (LED) curing unit in both immediately (55, 58) and after-1-week polymerizations (58). In the nanohybrid resin composite, the degree of conversion is 58.7% after light-cured 16 hours and the 70.4% degree of conversion after light-cured 30 days. (59).

The light curing polymerization is the exothermal reaction (60). Some studies measuring the degree of polymerization of dentin bonding agents via indirect measuring of the temperature. The dentin bonding agents of the three-step etch and rinse and two-step self-etch adhesives showed the peak of polymerization within 10-15 seconds. In the two-step etch and rinse and one-step self-etching adhesive, they took 30-50 seconds for polymerization (60) (Figure 11).

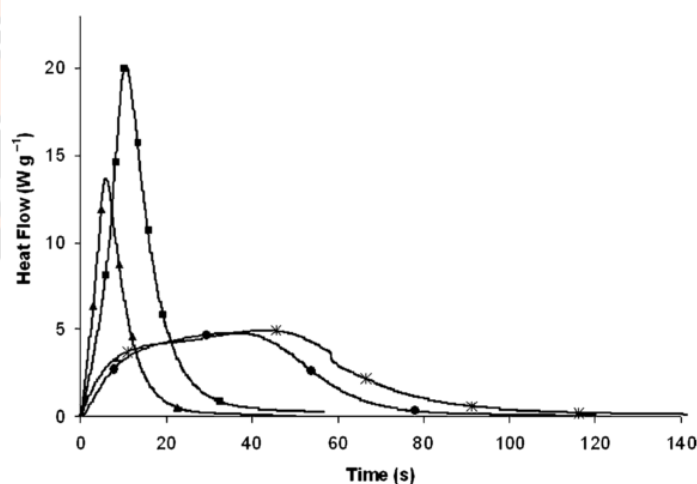


Figure 11 The time interval for polymerization of different dental bonding agents measured by differential scanning calorimetry (DSC) (60).

Note: ▲, Optibond FL; ●, One Step Plus; ■, Clearfil Protect Bond; and X, Xenio III.

The size of the monomer influences the releasing rate into the environment. The small-size monomers tend to detach easily from the adhesive layer (61, 62). The amount of the released residual monomer of the one-step self-etch adhesive was

highest at the first ten minutes. After that, the monomer release continues for 30 days (63). The light-exposure times, 10s, 20s, and 40s do not affect the quantity of the released monomers. The lowest amount of released monomers was found in the QTH (64). The type of light-curing unit affects the amount of the released residual monomer after polymerization.

The bond mechanism between the immediate dentin sealings and the dental adhesives of resin cement is similar to the repairing process of the aged resin composite restorations. This procedure depends on both mechanical and chemical adhesions. Mechanical adhesion is the significant mechanism. The etchant in the etch-and-rinse system and the priming agent in the self-etch system could remove debris covering the surface of the aged resin composite (65). The application of phosphoric acid on the aged resin composite before repairing could improve surface characteristics. Therefore, this process is recommended for routine resin composite repairment (59). Grinding with a diamond bur and air blasting technique are practically mechanical methods (66-69). Sandblasting with aluminum oxide is widely advised since this method is able to improve the bond strengths than others (68, 70-72). Surface treatment with applying the dental adhesive is also able to improve the bond strength of the repaired resin composite (73-75). This combined method could improve surface wettability (76) by facilitating the penetration of the new dental adhesives and creating the adhesive-resin micromechanical interlocking. Preparation of the aged resin composite is important to the success of repairing by increasing the surface area (77) and the wettability (78) of the aged materials.

The 2-hydroxyethylmethyl-acrylate (2-HEMA), the hydrophilic primer, improves the wettability of the aged composite materials, so the new dental adhesives could penetrate into the deep porosity area. When 2-HEMA copolymerizes with acetone or ethanol, the wettability will increase superiorly. The hydrophobic monomers in resin composite are bondable to the monomers in dental adhesives. There are 2 factors that determine the penetrating ability of dental adhesive into the resin composite such as the chemical affinity of the dental adhesive and the degree of hydration of resin composite (79, 80). Immediate repairment the resin composite receives higher bond strength than aged composite significantly for two-step etch-and-rinse and two-step self-etch adhesive. The immediate repairment of resin composite creates good adhesion. In 2011, 67% of the repaired resin composite got the adhesive failure at the interface between the aged resin composite and the new dental adhesive layer (81). Some studies suggested that the bond strength of repaired resin composite decreased was related to the water-saturated in the aged resin composite which affected the number of free radicals (68, 82).

The interface between the IDS and the dental adhesive of the resin cement is similar to resin composite repairment. After polymerization of the IDS, the unreacted monomers or residual monomers are removed for preventing the inhibition of the polymerization of the impression materials. The phosphoric acid or acidic primers were applied on this surface to increase the wettability to promote the adaptability of the new dental adhesives.

The IDS is an additional technique suggested to mainly prevent dentin hypersensitivity. As plenty of benefits from the immediate dentin sealing procedure, either etch-and-rinse or self-etch dental adhesive systems can use for this procedure. In the cementation procedure, it is unavoidable that the dental adhesives for the resin

cement contact to the IDS. Although they are clinically applied at different periods of time, the different dental adhesives might affect on the bond strength of resin cement.

The aim of this study is to investigate the effect of different kinds of dental adhesives between the IDS and the dental adhesive system of resin cement by observing the shear bond strength of the restorations which are cemented by the resin cement.



Chapter 3

Research Procedures of the Study

Specimen Preparation

One hundred and thirty sound human premolar teeth without cracks, restorations, or carious lesions, indicated extraction for the orthodontic treatment were selected in this study (NU-IRB No. 0685/62). Teeth were stored in 0.1% Thymol solution at room temperature and were used within 3 months after extraction. The teeth were fixed in the acrylic resins in the 20-mm diameter PVC pipes with mid coronal above PVC pipe 2 mm. The coronal half of the tooth was removed by the slow-speed diamond saw (Isomet 5000, Buehler Ltd., Illinois, USA) with water coolant to allow the total dentin exposure. The cut surfaces were finished with 600-grit silicon carbide paper for 1 minute with water to create smooth surface dentin and mimic the formation of the smear layer (61). The specimens were soaked in distilled water at 37 °C for 24 hours.

Immediate Dentin Sealing Application

The tooth specimens were randomly divided into thirteen groups (n=10) (Table 1) following the types of the immediate dentin sealing materials and resin cements. The immediate dentin sealing adhesives were applied on the dentin surface of the specimens followed the manufacturing instructions (Table 2 and 3). The thickness of the immediate dentin sealing layer was controlled by the microbrush. The new microbrush was used to wipe off and absorbed the excess bonding agent followed by polymerization for 10 seconds. After receiving the polymerization, the petroleum jelly (Vaseline, Unilever, Bangkok, Thailand) was applied with a thin layer on top of the immediate dentin sealing adhesive by the microbrush followed by additional polymerization for 10 seconds (50). The petroleum jelly and the oxygen inhibiting layer were eliminated by the cotton pellet with 70% ethyl alcohol and the 5-second polished by pumice with slow-speed handpiece 500 rpm (53).

Table 1 The group designed mainly considered the type of dental adhesives and resin cements

Group	Immediate dentin sealing	Resin cement
CSE-PV5	CLEARFIL™ SE BOND	PANAVIA™ V5
OXTR-PV5	OptiBond™ XTR	PANAVIA™ V5
PV5	-	PANAVIA™ V5
OXTR-OXRT/NX3	OptiBond™ XTR	OptiBond™ XTR + NX3 Nexus™
CSE-OXTR/NX3	CLEARFIL™ SE BOND	OptiBond™ XTR + NX3 Nexus™
OXTR/NX3	-	OptiBond™ XTR + NX3 Nexus™
OXTR-SCB	OptiBond™ XTR	Super-Bond C&B
CSE-SCB	CLEARFIL™ SE BOND	Super-Bond C&B
SCB	-	Super-Bond C&B
SBU-SBU/RU(TE) (Etch-and-rinse mode)	Single Bond Universal Adhesive	Single Bond Universal Adhesive + RelyX™ Ultimate™
SBU/RU(TE) (Etch-and-rinse mode)	-	Single Bond Universal Adhesive + RelyX™ Ultimate™
SBU-SBU/RU(SE) (Self-etch mode)	Single Bond Universal Adhesive	Single Bond Universal Adhesive + RelyX™ Ultimate™
SBU/RU(SE) (Self-etch mode)	-	Single Bond Universal Adhesive + RelyX™ Ultimate™

Table 2 The compositions of each material in this study

Material	Category	Manufacturer	Batch number	Composition
Single Bond Universal Adhesive	Light-cure universal bonding agent	3M ESPE	81219B	MDP Phosphate Monomer, dimethacrylate resins HEMA, Vitrebond™ Copolymer, filler, ethanol, water, initiators, silane
OptiBond™ XTR	Light-cure bonding agent (2-bottle self-etch)	KERR	7016650	Primer: GPDM (glycero-phosphate dimethacrylate), mono and di-functional methacrylate monomers, camphorquinone, water, ethanol, and acetone Adhesive: Hydrophobic monomers, camphorquinone, barium glass and nano-silica and sodium hexafluorosilicate in ethanol
CLEARFIL™ SE BOND	Light-cure bonding agent (2-bottle self-etch)	Kuraray	000049	Primer: dimethacrylate monomer, MDP, HEMA, water, catalyst Adhesive: MDP, HEMA, dimethacrylate monomer, microfiller, catalyst
RelyX™ Ultimate™	Dual-cure resin cement	3M ESPE	4804925	Base paste: methacrylate monomers, radiopaque, silanated fillers, initiator components, stabilizers, rheological additives Catalyst Paste: methacrylate monomers, radiopaque alkaline (basic) fillers, initiator components, stabilizers, pigments, rheological additives, fluorescence dye, dual-cure activator for Single Bond Universal Adhesive
NX3 Nexus™ cement	Dual-cure resin cement	KERR	7055976	Glass, oxide, ytterbium trifluoride, poly(oxy-1,2-ethanediyl), diazahexadecane-1,16-diyl bismethacrylate, ethylenedioxydiethyl dimethacrylate, 2-hydroxyethyl methacrylate, silanamine, 1,1,1-trimethyl-N-(trimethylsilyl)-, hydrolysis products with silica, and trimethoxysilylpropyl methacrylate
PANAVIA™ V5	Dual-cure resin cement (Self-etch)	Kuraray	000062	Tooth primer: Phosphonate, MDP, HEMA, hydrophilic aliphatic dimethacrylate, accelerators, water Restoration primer: MDP monomer, silane monomer Adhesive: Bis-GMA, TEGDMA, hydrophobic aromatic dimethacrylate, hydrophilic aliphatic dimethacrylate, Initiators, accelerators, silanated barium glass filler, silanated fluoroaluminosilicate glass filler, colloidal silica, silanated aluminium oxide filler, dl camphorquinone, pigments
Super-Bond C&B	Self-cure resin cement (Etch-and-rinse)	Sun Medical	TF2	Catalyst V: Partially oxidized Tri-n-butylborane, others Monomer: Methacrylate monomers, others. Quick Monomer: Methacrylate monomers, others Polymer: Polymethyl methacrylate, others. Red Activator: Phosphoric acid, Water, others. Green Activator: Citric acid, Ferric chloride, Water, others.

Table 3 Manipulation of dental adhesives, resin cements and resin composite

Materials	Handling
Single bond Universal Adhesive	Etch-and-rinse mode: Additional etched with 37% phosphoric acid 15s and rinsed off, gentle air blew 5 seconds before applying dental adhesive. Self-etch mode: Applied the adhesive to the dentin. Scrubbed the surface with a brushing motion for 20 seconds. Gentle air dried the adhesive for approximately 5 seconds to evaporate the solvent. Light cured for 10 seconds.
OptiBond™ XTR	- Applied OptiBond™ XTR PRIMER to the dentin surface using microbrush. Scrubbed the surface with a brushing motion for 20 seconds. Aired thin for 5 seconds with medium air pressure. - Shake OptiBond™ XTR ADHESIVE bottle briefly. Applied OptiBond™ XTR ADHESIVE to the dentin surface with light brushing motion for 15 seconds. Aired thin for 5 seconds. Light cured for 10 seconds.
CLEARFIL™ SE BOND	- Applied primer for 20 seconds. Dried with mild air for 5 seconds - Applied mixture of BOND. Gentle air flowed. Light cured for 10 seconds.
RelyX™ Ultimate™	- Mounted mixing tip to RelyX™ Ultimate Automix Syringe and discarded the initial amount. - Applied a uniform layer of RelyX™ Ultimate Adhesive Resin Cement to the restoration. - Seated and tagged light cure 1 second, removed excess cement. - Light cured 20 seconds each surface. * The manufacturer recommended to use with Adper™ Scotchbond™ Multi-Purpose or Adper™ Single Bond.
NX3 Nexus™ cement	- Dispensed NX3 cement (light-cure or dual-cure) directly into the indirect restoration. - Seated and tagged light cure several seconds, removed excess cement. - Light cured 20 seconds each surface. * The manufacturer recommended to use with OptiBond™ XTR.
PANA VIA™ V5	- Applied CERAMIC PRIMER PLUS and dried into inner surface of the resin composite restoration. - Applied Tooth Primer at tooth surface, leaved for 20 seconds and dried. - Dispensed cement and placed the restoration. - Seated and tagged light cure 3-5 seconds, removed excess cement. - Light cured 20 seconds each surface.
Super-Bond C&B	Bulk-mix technique - Applied with the Green Activator for 10 seconds at the tooth surface, rinsed off and gentle air blew 5 seconds - Mixed catalyst, monomer, and polymer with ratio 1:4:1 applied the adhesive mixture to the surfaces before the polymerization reaction advances, and positioning the surfaces and holding them immobile with the fingers till the curing reaction was completed (8 minutes). - Removed excess cement. - Left it in a dry area for 30 minutes and then placed the specimen in distilled water.

Resin Composite Fabrications and Surface Treatment

The teflon mold with 4.5 mm diameter and 2 mm height was placed on a coverslip. The resin composite (Ceram. X[®] SphereTec[™] one, Densply, Surrey, United Kingdom) was filled in the mold, covered by another coverslip before polymerization for 20 seconds. After taking the mold off, the resin composite was continuously cured for 20 seconds on each surface by the LED curing unit (Mini LED[™]; Acteon, France), with 1,250 mW/cm² light intensity. Before cementation, the adhesive surface of each resin composite bar was subjected to 50- μ m aluminium oxide abrasive powder (Prophyflex 3, KaVo, Biberach, Germany) with a distance of 5 mm, pressure 3.2 for 5 seconds for increasing the surface roughness. All specimens were then being cleaned by ultrasonic at 40 kHz for 5 minutes (62).

Resin Cement Applications

Each resin composite was used followed the company instruction for cementing the resin composite rods. Each resin composite rod was seated with 5 N finger pressure by one operator (62), followed by 20 seconds light curing for resin cement polymerization. After cementation, the specimens were stored in water at 37 °C for 24 hours. All specimens were then undergone thermocycling (SDC20, Yamatake Honeywell, HWB332R) between 5 °C and 55 °C with 15 s dwelling time for 5,000 cycles (63, 64).

Investigation the Bond Strength

The specimens were subjected to the shear force by a universal testing machine (Instron Universal Tester, model E1000, Instron Inc, Canton, MA, USA) in distilled water at 37 °C. The dentin surfaces of the specimens were positioned parallel to the direction of a force. A chisel-liked loading head was loaded at the dentin-resin composite interface with the cross head speed 1 mm per minute until failure occurred (ISO/TS 11405) (65).

Before the failure mode analysis, all kinds of substances; dentin, dental adhesives and resin cements, were preliminarily investigated under the scanning electron microscope (SEM) (LEO 1455 VP; Carl Zeiss SMT AG, Oberkochen, Germany). An energy dispersive X-ray analysis (EDX) was used to differentiate the layer of specimens.

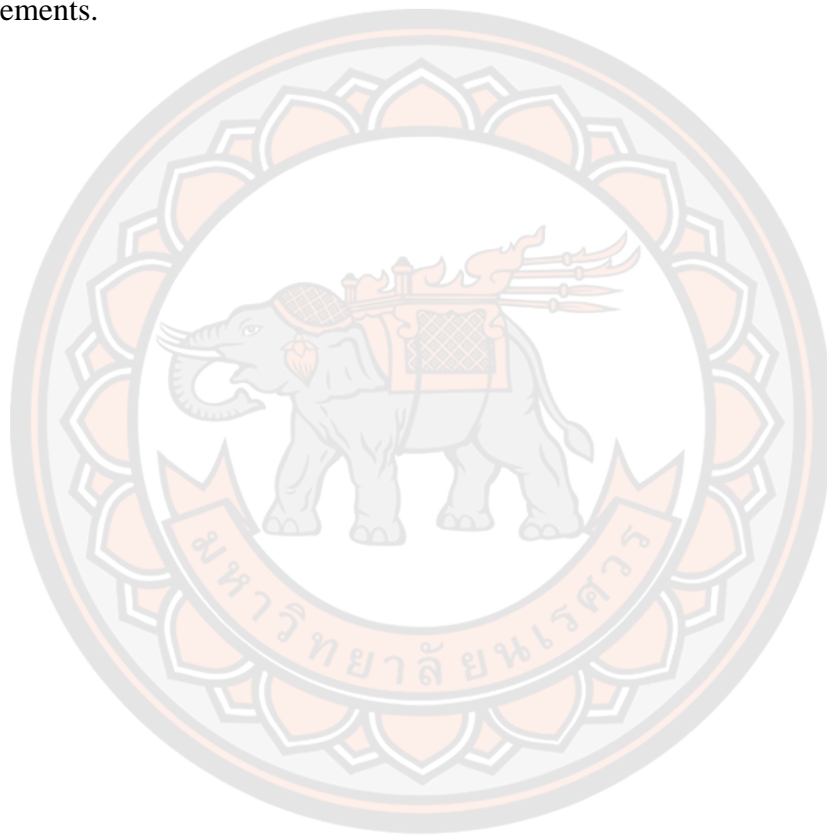
The fracture surfaces of each specimen were observed under the SEM with the magnification x3,000 and x10,000 to identify the type of failure. The failure mode was classified as:

- adhesive failure between dentin and immediate dentin sealing
- adhesive failure between immediate dentin sealing and bonding agent
- adhesive failure between immediate dentin sealing and resin cement
- adhesive failure between bonding agent and resin cement
- adhesive failure between resin cement and resin composite
- cohesive failure in dentin
- cohesive failure in bonding agent

- cohesive failure in resin cement
- cohesive failure in resin composite

Data Analysis

The average shear bond strength data had a normal distribution. The One-way ANOVA was computed at the confidence level of 95%. This study investigated the shear bond strength of the three main groups. The first group was no immediate dentin sealing or baseline. The second group was the immediate dentin sealings with the similar composition to the adhesive system of resin cements. The third group was the immediate dentin sealings with different compositions to the adhesive system of resin cements.



Chapter 4

Results

This study observed the shear bond strength of the restorations when applying different resin cements. In each resin cement was also compared the shear bond strength among no IDS and with IDS groups. In the with IDS groups, they are divided to be applying IDS with the similar composition of the dental adhesives (same company as the resin cement) and with different composition of the dental adhesives (different company of the resin cement).

According to types of resin cements; PANA VIA™ V5, NX3 Nexus™, Super-Bond C&B and RelyX™ Ultimate™, the shear bond strength are vary. In the PANA VIA™ V5 resin cement and the Super-Bond C&B resin cement, there was no significant difference among groups in each kind of resin cement. When using the resin cement with or without IDS, there was no statistical difference in the shear bond strength of the restorations.

In the NX3 Nexus™ resin cement, when applied the similar-composition IDS (OXTR-OXTR/NX3), the shear bond strength significantly higher than the non-IDS group (OXTR/NX3). When applied different-composition IDS (CSE-OXTR/NX3), the shear bond strength slightly increased with no significant difference from both non-IDS and similar-composition IDS.

The RelyX™ Ultimate™ resin cement is recommended to use along with the Single Bond Universal Adhesive. The Single Bond Universal Adhesive was also applied as the IDS in this groups. When applied this IDS with either etch-and-rinse technique or self-etch technique, the shear bond strength was not different from non-IDS groups.

Regarding the non-IDS groups, the RelyX™ Ultimate™ resin cement along with the Single Bond Universal Adhesive with either etch-and-rinse technique or self-etch technique, there was no statistical difference between them. In addition, this resin cement also provided the highest shear bond strength compared to other types of resin cement. PANA VIA™ V5 is the second place of the highest shear bond strength. It was significantly lower than the RelyX™ Ultimate™ resin cement. NX3 Nexus™ resin cement and Super-Bond C&B resin cement had insignificant difference shear bond strength, which was lowest among these four resin cements.

When applying IDS with the similar composition to the adhesive system of resin cements, there were insignificantly differences in shear bond strength when compared to a non-IDS of each resin cement, except the NX3 Nexus™ resin cement (OXTR-OXTR/NX3). The shear bond strength of this group increased to be able to compare to the RelyX™ Ultimate™ resin cement and PANA VIA™ V5 resin cement.

When applying IDS with the different components to the adhesive system of resin cement, there were insignificant differences in shear bond strength when compared to non-IDS of each resin cement and among resin cement.

Table 4 Mean shear bond strength of resin cement with and without IDS

Group	Resin cement	IDS	SBS
			Mean (MPa) \pm SD
CSE-PV5	Panavia V5	Clearfil SE	15.13 \pm 3.24 ^{a CE}
OXTR-PV5	Panavia V5	Optibond XTR	11.88 \pm 4.63 ^{a CD}
PV5	Panavia V5	No	11.05 \pm 1.88 ^{a AFH}
OXTR-OXTR/NX3	NX3 Nexus	Optibond XTR	12.90 \pm 3.88 ^{bc CEFI}
CSE-OXTR/NX3	NX3 Nexus	Clearfil SE	7.83 \pm 3.14 ^{ac ADG}
OXTR/NX3	NX3 Nexus	No	4.78 \pm 2.40 ^{a B}
OXTR-SCB	Superbond C & B	Optibond XTR	5.49 \pm 3.37 ^{a AB}
CSE-SCB	Superbond C & B	Clearfil SE	8.47 \pm 4.51 ^{a BDHI}
SCB	Superbond C & B	No	9.10 \pm 3.67 ^{a BG}
SBU-SBU/RU(TE) (Etch-and-rinse mode)	Rely X Ultimate (TE)	Single Bond Universal	13.97 \pm 3.56 ^{a CEH}
SBU/RU(TE) (Etch-and-rinse mode)	Rely X Ultimate (TE)	No	17.76 \pm 4.29 ^{a CE}
SBU-SBU/RU(SE) (Self-etch mode)	Rely X Ultimate (SE)	Single Bond Universal (SE)	15.41 \pm 3.19 ^{a CEF}
SBU/RU(SE) (Self-etch mode)	Rely X Ultimate (SE)	No	16.67 \pm 2.67 ^{a E}

Lower case: Statistic significance within group ($p < 0.05$).

Upper case: Statistic difference between groups ($p < 0.05$).

The characteristic of all reagents in this study was investigated by scanning electron microscope (SEM) as illustrated in figure 12-17. Generally, the filler particles of dental adhesive were smaller than that of the resin cement and the resin composite. The Ceram.x[®] SphereTec[™] One had two sizes of filler particles; SphereTEC filler larger than 1 micrometer ($\sim 3.5\mu\text{m}$) and sub-micron glass filler particles. The filler density in the dental adhesives was also lower than the resin cement and resin composite. Therefore the dental adhesives were able to be distinguished from the resin cements and the resin composite. Although resin composite and resin cements had a similar density of the filler particles, they could be distinguished by their individual characteristics of filler particles.

The SEM pictures showed the characteristics of all reagents in each group. They were used as the baseline to consider the failure modes in this study as showed in figure 12-13.

Applied as IDS on dentin surface

Dental adhesive rod

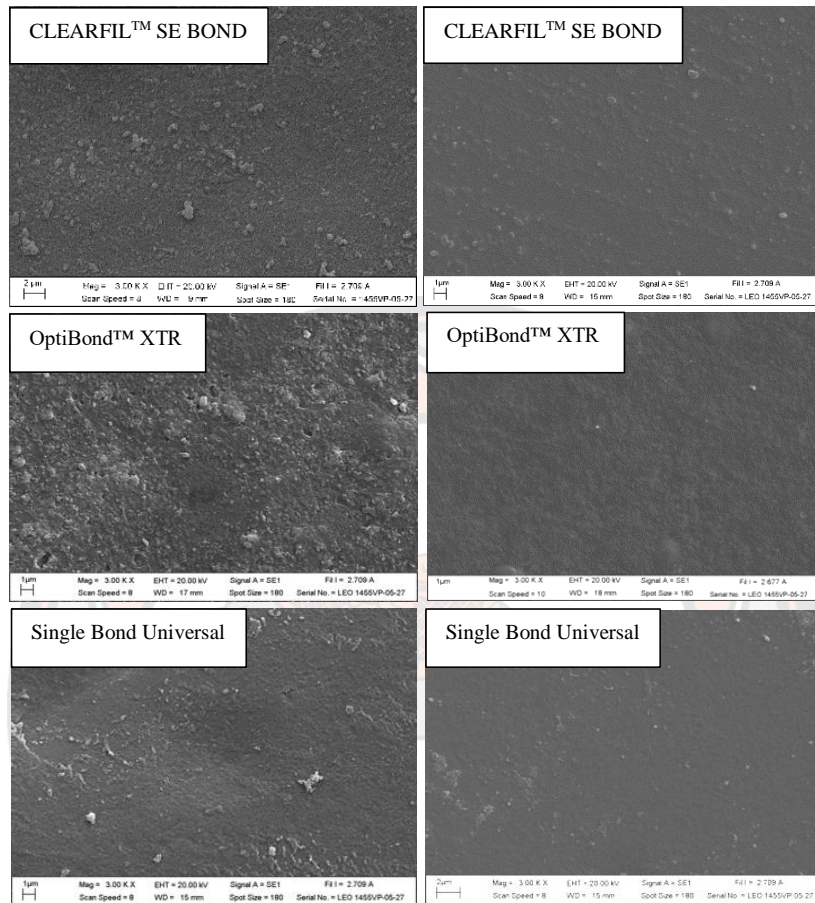


Figure 12 The SEM (X3000) of the dental adhesives applied on dentin surfaces (left column) and the dental adhesive rods (right column).

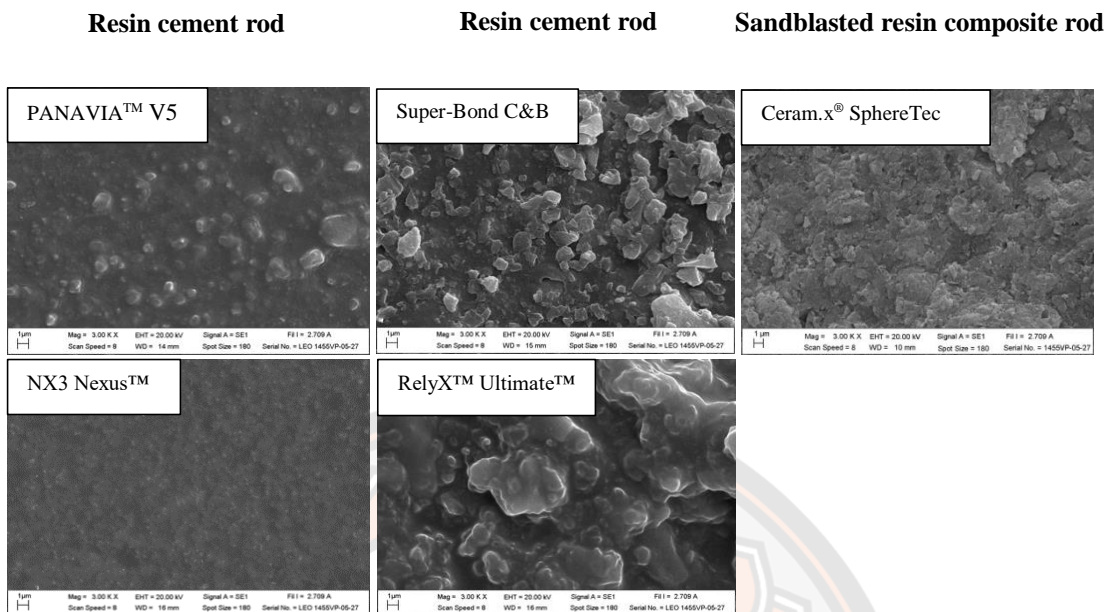
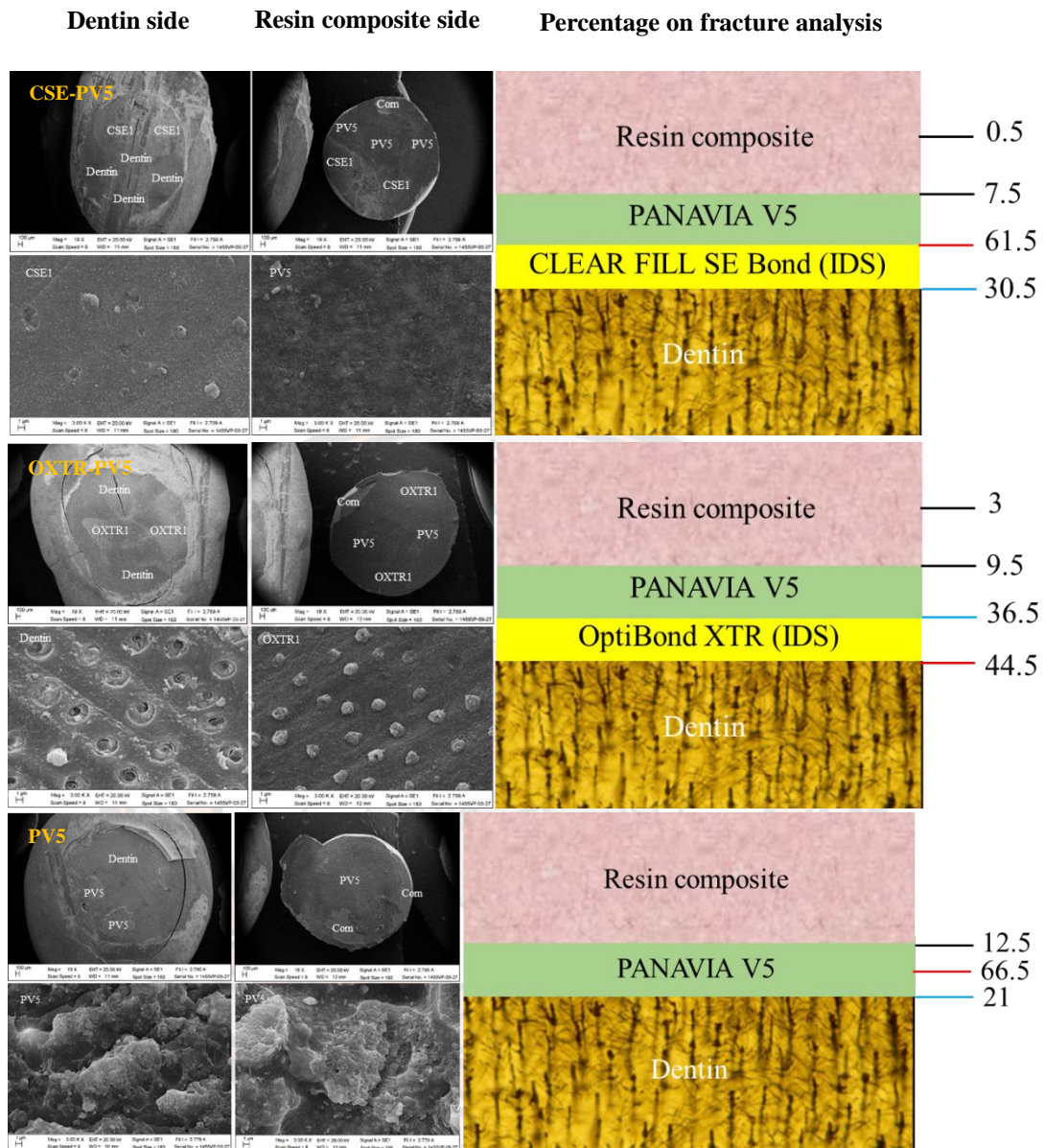


Figure 13 The surface characteristic of resin cements and resin composite by SEM (x3000).

The PANAVIA™ V5, Super-Bond C&B, and RelyX™ Ultimate™ show the large filler particles. The NX3 Nexus™ has fine filler particles.

Failure mode analysis of debonded specimens in each group presented in Figure 14-18. Failures in the PANAVIA™ V5 resin cement (CSE-PV5, OXTR-PV5, and PV5) presented in different locations (figure 14). Most of the specimens in the CSE-PV5 group showed 61.5% adhesive debonds between the immediate dentin sealing and the adhesive layer of the resin cement. The OXTR-PV5 group showed 44.5% adhesive failure between the dentin and the immediate dentin sealing. On the other hand, the majority failure of the PV5 group occurred as a cohesive failure.



Note: OXTR1 = OptiBond™ XTR (IDS), CSE1 = CLEAR FILL™ SE Bond (IDS), PV5 = PANAVIA™ V5

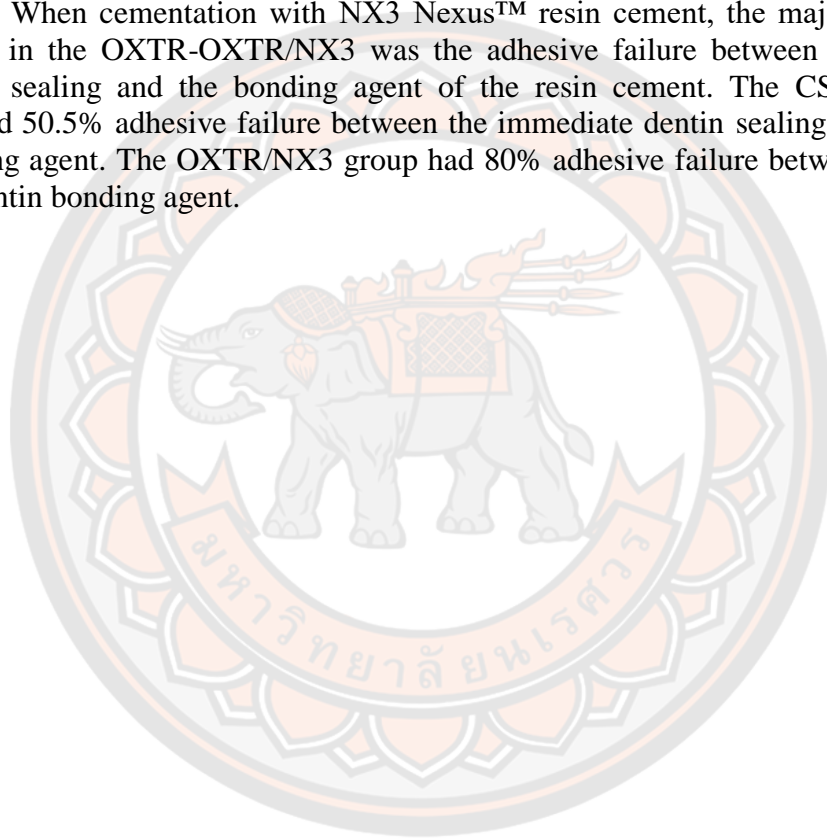
Figure 14 The failure mode characteristics of the cementation with the PANAVIA™ V5 resin cement groups.

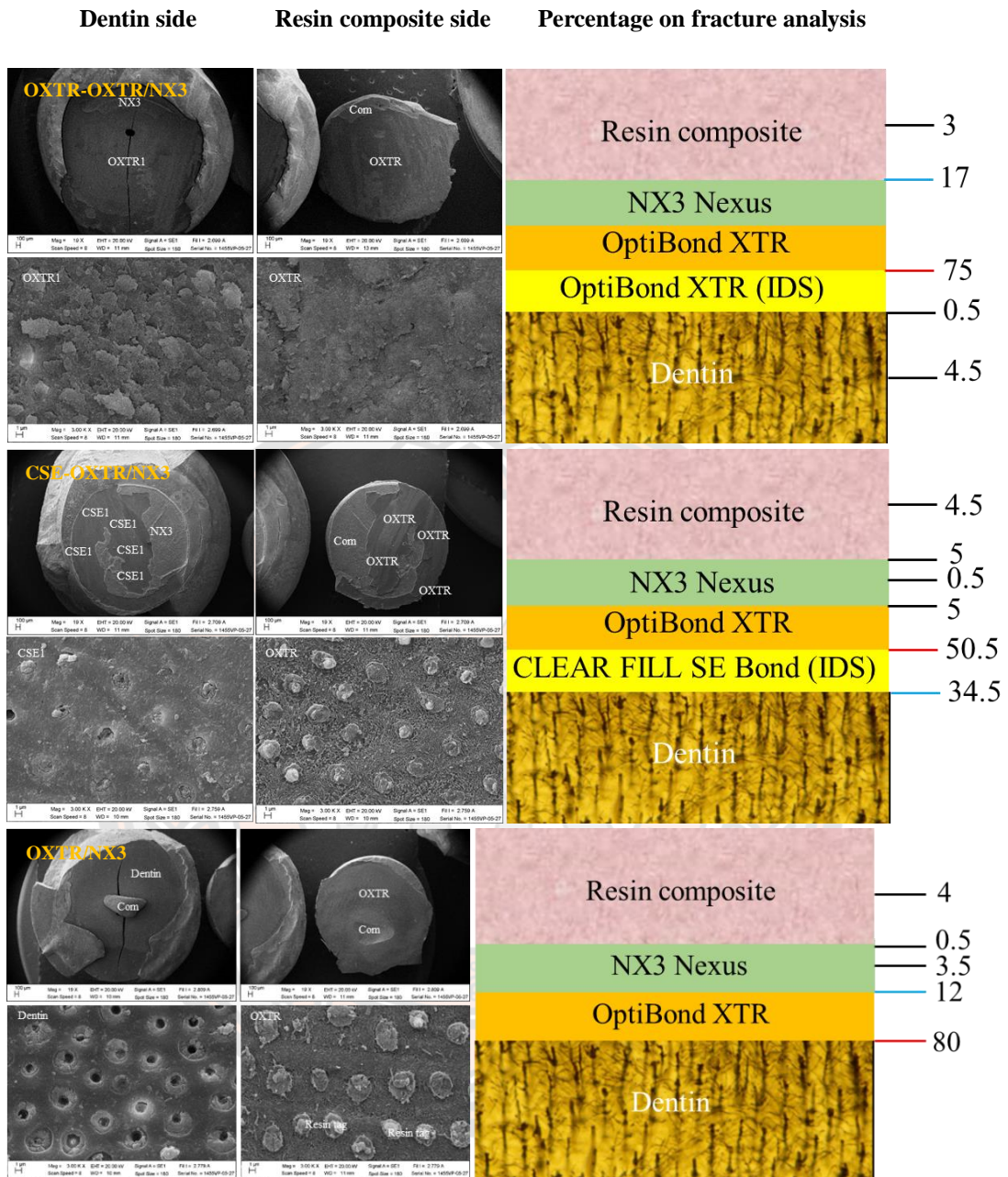
In the CSE-PV5 group, the adhesive failure between IDS and dentin bonding agent is the highest percentage of failure modes, 61.5%. The low magnification figures show the fracture patterns on both tooth side and resin composite side. In the high magnification figures, the hybrid layer of the CLEAR FILL™ SE Bond (IDS) still attaches to tooth together with most of the resin tags. The PANAVIA™ V5 attaches to the resin composite side.

In the OXTR-PV5 group, the adhesive failure between dentin and immediate dentin sealing is the majority failure mode, 44.5%. The low magnification figures show the fracture patterns on the tooth side and resin composite side. In the high magnification figures, almost most all resin tags with a hybrid layer of the OptiBond™ XTR bind to the resin composite side.

In the PV5 group, the cohesive failure in the resin cement (PANAVIA™ V5) is the majority failure mode, 66.5%. The low magnification figures show the fracture patterns on both the tooth side and resin composite side. In the high magnification figures, the PANAVIA™ V5 is found on both tooth side and the resin composite side.

When cementation with NX3 Nexus™ resin cement, the majority of failure (75%) in the OXTR-OXTR/NX3 was the adhesive failure between the immediate dentin sealing and the bonding agent of the resin cement. The CSE-OXTR/NX3 showed 50.5% adhesive failure between the immediate dentin sealing and the dentin bonding agent. The OXTR/NX3 group had 80% adhesive failure between dentin and the dentin bonding agent.





Note: OXTR1 = OptiBond™ XTR (IDS), OXTR = OptiBond™ XTR, CSE1 = CLEAR FILL™ SE Bond (IDS), RU = RelyX™ Ultimate™, NX3 = NX3 Nexus™ Third Generation Cements

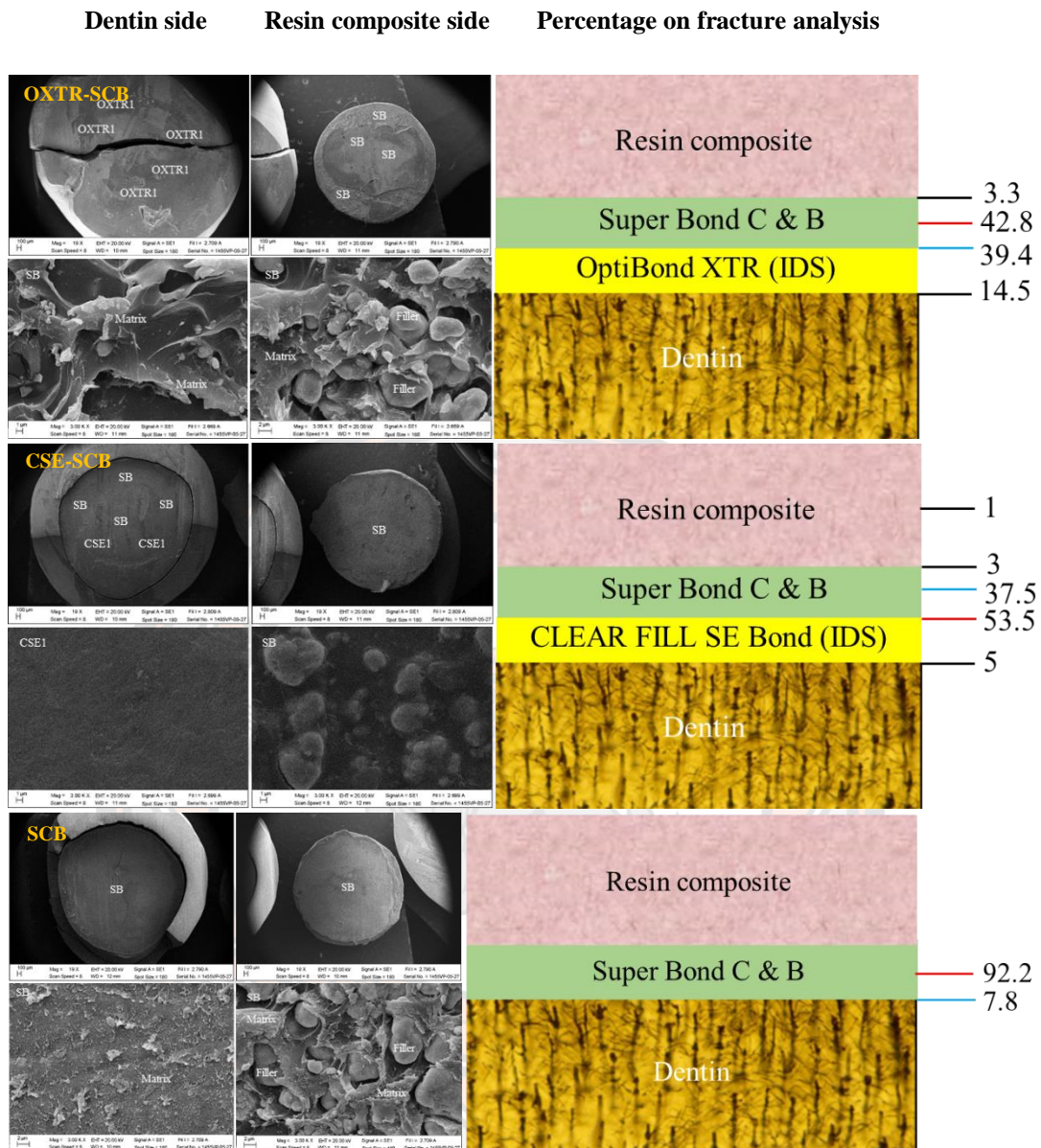
Figure 15 The failure mode characteristics of the cementation with the NX3 Nexus™ resin cement groups.

In the OXTR-OXTR/NX3 group, the adhesive failure between IDS and dentin bonding agent is the highest percentage of failure modes, 75%. The low magnification figures show the fracture patterns on both tooth side and resin composite side. In the high magnification figures, the hybrid layer of the OptiBond™ XTR (IDS) still attaches to the tooth side together with most of the resin tags. Another layer of OptiBond™ XTR adhesive is found on the resin composite side.

In the CSE-OXTR/NX3 group, the adhesive failure between the CLEAR FILL™ SE Bond (IDS) and the dentin bonding agent (OptiBond™ XTR) is the majority failure mode, 50.5%. The low magnification figures show the fracture patterns on both the tooth side and resin composite side. In the high magnification figures, the hybrid layer of the CLEAR FILL™ SE Bond (IDS) attaches to the tooth side while the OptiBond™ XTR attaches to the resin composite.

In the OXTR/NX3 group, the adhesive failure between dentin and dentin bonding agent is the majority failure mode, 80%. The low magnification figures show the fracture patterns on both the tooth side and resin composite side. In the high magnification figures, the dentinal tubule pattern is presented with a couple of resin tags. A large number of the OptiBond™ XTR resin tags and the hybrid layer bind to the resin composite side.

The failures of the cementation with Super-Bond C&B resin cement (OXTR-SCB, CSE-SCB, and SCB) were shown in Figure 16. The majority of failure in the OXTR-SCB group was the cohesive failure in the resin cement while the adhesive failure between the immediate dentin sealing and the resin cement was the majority failure in the CSE-SCB group. The majority failure in the SCB group was the cohesive failure in the resin cement.



Note: OXTR1 = OptiBond™ XTR (IDS), OXTR = OptiBond™ XTR, CSE1 = CLEAR FILL™ SE Bond (IDS), SB = Super Bond C&B

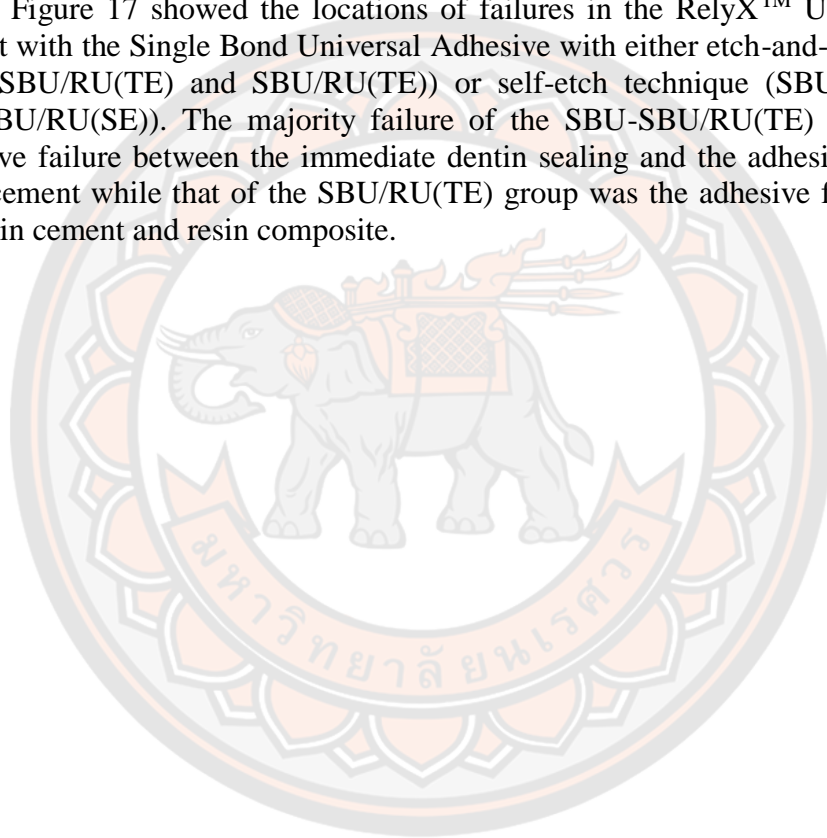
Figure 16 The failure mode characteristics of the cementation with the Super-Bond C&B resin cement groups.

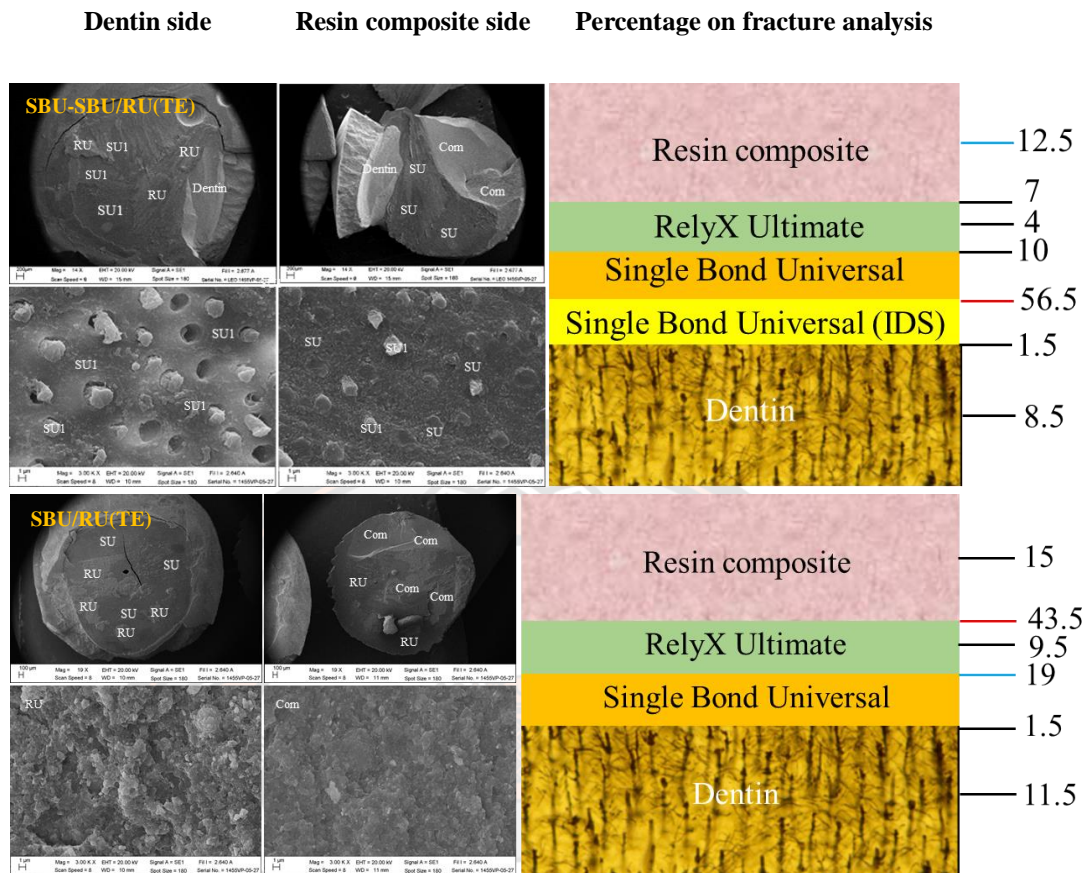
In the OXTR-SCB group, the cohesive failure in resin cement (Super Bond C & B) is the majority failure mode, 42.8%. The low magnification figures show the fracture patterns on both the tooth side and resin composite side. In the high magnification figures, the fracture within the Super Bond C & B shows the separation of the resin matrix and fillers.

In the CSE-SCB group, the adhesive failure between the IDS and resin cement is the majority failure mode, 53.3%. The low magnification figures show the fracture patterns on both the tooth side and resin composite side. In the high magnification figures, the hybrid layer of the CLEAR FILL™ SE Bond (IDS) attaches to the tooth side. The Super Bond C & B attaches to the resin composite side.

In the SCB group, the cohesive failure in the resin cement (Super Bond C & B) is the majority failure mode, 92.2%. The low magnification figures show the fracture patterns on both the tooth side and resin composite side. In the high magnification figures, the matrices of the Super Bond C & B attach on the tooth side.

Figure 17 showed the locations of failures in the RelyX™ Ultimate™ resin cement with the Single Bond Universal Adhesive with either etch-and-rinse technique (SBU-SBU/RU(TE) and SBU/RU(TE)) or self-etch technique (SBU-SBU/RU(SE) and SBU/RU(SE)). The majority failure of the SBU-SBU/RU(TE) group was the adhesive failure between the immediate dentin sealing and the adhesive layer of the resin cement while that of the SBU/RU(TE) group was the adhesive failure between the resin cement and resin composite.





Note: TE = etch-and-rinse mode, SU1 = Single Bond Universal Adhesive (IDS), SU = Single Bond Universal Adhesive, RU = RelyX™ Ultimate™

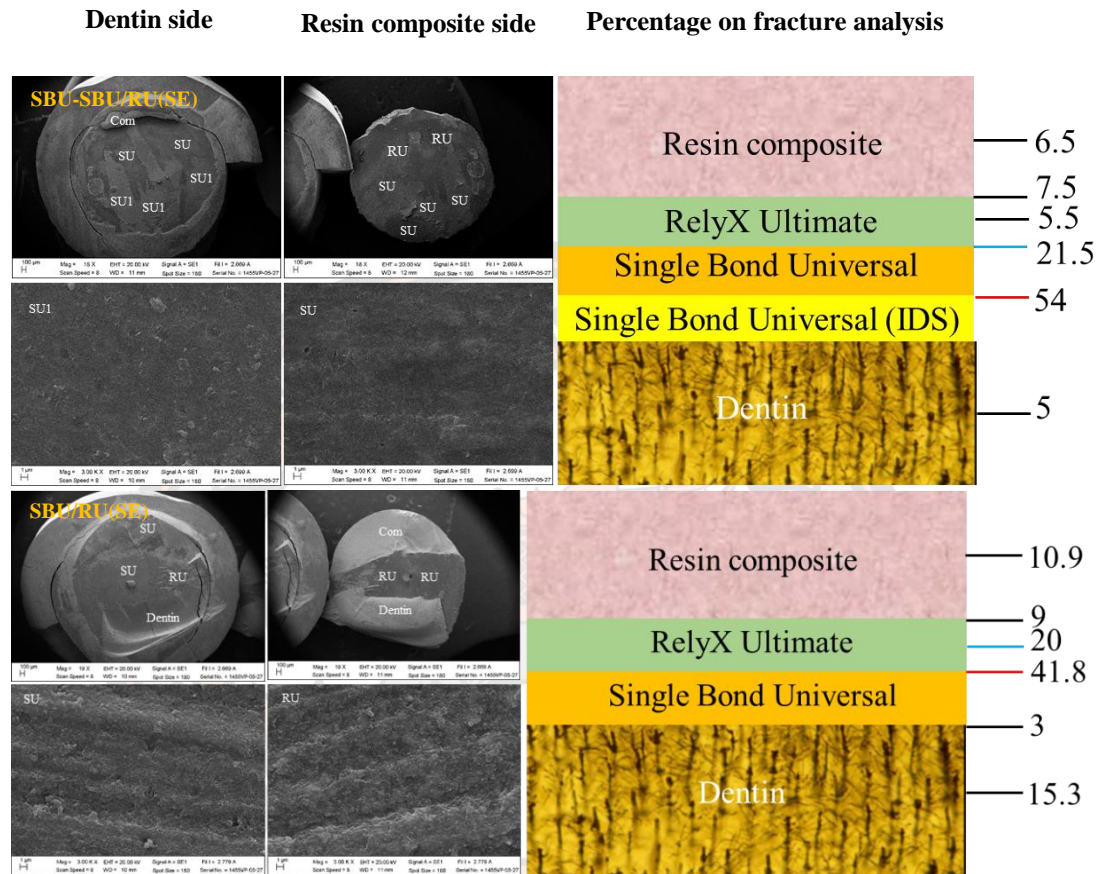
Figure 17 The failure mode characteristics of the cementation with the RelyX™ Ultimate™ resin cement in etch-and-rinse mode.

In the SBU-SBU/RU(TE) group, the adhesive failure between IDS and dentin bonding agent is the highest percentage of failure modes, 56.5%. The low magnification figures show the fracture patterns on the tooth side and resin composite side. In the high magnification figures, the hybrid layer of the Single Bond Universal Adhesive (IDS) still attaches to the tooth surface together with some resin tags. Some resin tags detach and bind to the resin composite rod.

In the SBU/RU(TE) group, the adhesive failure between resin cement and resin composite is the majority failure mode, 43.5%. The low magnification figures show the fracture patterns on both the tooth side and resin composite side. In the high magnification figures, the RelyX™ Ultimate™ attaches to the tooth side. The sandblasted resin composite surface is shown on the resin composite side.

Figure 18 showed the locations of failures in the Single Bond Universal Adhesive applied with the self-etched mode (SBU-SBU/RU(SE) and SBU/RU(SE)). The SBU-SBU/RU(SE) group had the adhesive failure as the major failure between

the immediate dentin sealing and the adhesive layer of the resin cement while that of the SBU/RU(SE) group had the adhesive failure between the dentin bonding agent and the resin cement.



Note: TE = self-etched mode, SU1 = Single Bond Universal Adhesive (IDS), SU = Single Bond Universal Adhesive, RU = RelyX™ Ultimate™

Figure 18 The failure mode characteristics of the cementation with the RelyX™ Ultimate™ resin cement in self-etch mode.

In the SBU-SBU/RU(SE) group, the adhesive failure between IDS and dentin bonding agent is the highest percentage of failure modes, 54%. The low magnification figures show the fracture patterns on tooth side and resin composite side. In the high magnification figures, the hybrid layer of the Single Bond Universal Adhesive (IDS) attaches to the tooth surface, whereas another Single Bond Universal Adhesive is found on the resin composite side.

In the SBU/RU(SE) group, the adhesive failure between dentin bonding agent and resin cement is the highest percentage of failure mode, 41.8%. The low magnification figures show the fracture patterns on both the tooth side and resin composite side. In the high magnification figures, the hybrid layer of Single Bond Universal Adhesive attaches on the tooth side. The RelyX™ Ultimate™ binds to the resin composite side.

Chapter 5

Discussion and Conclusion

Discussion

Single Bond Universal adhesive was only one universal adhesive in this study. The methacrylate modified polyalkenoic acid or Vitrebond Copolymer (VBCP) is a key component of Single Bond Universal adhesive, which has been studied to support both increasing and decreasing bond strength. The universal adhesive, which contains the VBCP, had higher bond strength than the non-VBCP adhesive (66). The VBCP improved bond strength by promoting chemical bonds in nanolayering structures (67). On the other hand, some studies found lower bond strength in the VBCP-contained adhesives than the non-VBCP adhesive. The VBCP competed with the 10-MDP functional monomer to bind the Ca-binding site of hydroxyapatite (31, 68), and the VBCP had a high molecular weight, therefore it prevented polymerization of the dental adhesive (68). Another component that improved bondability is the silane coupling agent (17). After silane is hydrolyzed to silanol, the silanol group molecules function as an intermediate reagent by forming a polysiloxane network to bond to both the resin matrix and glass filler particles of either dentin substrate or resin-based materials.

This study corresponded to the previous studies (69, 70) that there was no difference in shear bond strength when applying the Single Bond Universal Adhesive in either etch-and-rinse or self-etch techniques. Even after thermocycling for 6 months, their shear bond strengths were not different (71). However there were some studies showed higher μ TBS of self-etch mode compared to the etch-and-rinse mode (72). Applying the phosphoric acid over time caused the adhesive unable to flow into the deeper dentinal tubule. This would affect chemical binding (30, 73-76). The Single Bond Universal Adhesive is the dental adhesives which the company recommends using along with the RelyX™ Ultimate™ resin cement.

CLEARFIL™ SE BOND dental adhesive containing 10-methacryloxydecyl dihydrogen phosphate (10-MDP) functional monomer had the chemical interaction with the hydroxyapatite along with the demineralized tooth structure forming the MDP-Ca salt complex. After the phosphate group of 10-MDP bound to the dentin, the methacrylate group away from the MDP-treated surface causing this surface became hydrophobic. The nanolayering is created from the parallel alignment of the several long carbon chain spacers (26). This monomer had strong ionic bonds to the tooth structure. From the TEM, the MDP-Ca complex presented nano-layering architecture (25). This complex structure was stable and durable, so it had higher withstanding to the hydrolysis compared to other functional monomers (30).

OptiBond™ XTR dental adhesive containing Glycerophosphate Dimethacrylate (GPDM) is a phosphate acidic monomer with one phosphate acidic functional group and two polymerizable methacrylate groups. It was able to

chemically bond to the dentin. This functional monomer was a small molecule with more hydrophilicity due to the short carbon chain (26). The GPDM was similar to the HEMA and that makes it easily penetrated into the demineralized dentin. The GPDM created a thick hybrid layer, and it had no nano-layering appearance (26). The GPDM molecule might be more hydrophilic than the MDP molecule, there was a less hydrophobic carbon chain spacer when compared with the MDP molecule. The manufacturer recommended using with OptiBond™ XTR adhesive along with the NX3 Nexus™ resin cement.

Braga et al. found that bond strength was correlated with the mode of polymerization and the compositions of resin cements (77, 78). After thermocycling, the cemented ceramic rod with Super-Bond C&B resin cement to dentin showed significantly lower shear bond strength (1.7 ± 0.4 MPa) when compared with other dual-cured resin cement (Variolink II and Panavia F) (79). When compared the microtensile bond strength between RelyX™ Ultimate™ resin cement (37.6 ± 6.0 MPa, 28.8 ± 4.7 MPa) and PANA VIA™ V5 resin cement (55.5 ± 5.1 MPa, 52.6 ± 4.8 MPa) (80), PANA VIA™ V5 resin cement had higher stability bond strength in long term aging (5,000 and 10,000 cycles) ($p < 0.05$). The RelyX™ Ultimate™ resin cement showed lower bond strength than PANA VIA™ V5 resin cement on both aging periods (80). This might be from the 10-MDP Ca-salt complex that was able to resist the hydrolytic degradation. As a result of this study, the decrease in shear bond strength of the RelyX™ Ultimate™ resin cement was not found even after aging for 5,000 cycles when used the RelyX™ Ultimate™ resin cement along with the Single Bond Universal Adhesive. The 10-MDP in the Single Bond Universal Adhesive might create more stable bond strength from the 10-MDP Ca-salt complex.

This study found that the shear bond strength of the OXTR/NX3 (no IDS) group was lower than others significantly. This finding agreed with a previous study in that GPDM-hydroxyapatite (GPDM-HAP) complex was not stable. It was dissolved in water easily when compared with the 10-MDP-HAP (26). In the μ TBS studies, there was no significant difference among GPDM, MDP functional monomer, and MDP-universal adhesive in self-etch mode (81). In 2015, the shear bond strength of the NX3 Nexus™ resin cement was around 3-5 MPa when cemented ceramic blocks (82), and it was similar to that in this study, (4.78 ± 2.40 MPa). The advantage of the NX3 Nexus™ resin cement is it has an amine-free redox system. This system can resist the unreacted acidic monomer in the oxygen inhibited layer, which leads to the damages of the bond structure between the adhesive layer and another resin-based substrate.

There were several studies found that applying the hydrophobic adhesive as the immediate dentin sealing could strengthen the bond strength. This layer was likely to be a hydrophobic layer preventing the hydrolytic degradation by water (55-57). However, this study showed significantly improved bond strength only in the NX3 Nexus™ resin cement when added IDS with a similar composition of the dental adhesives ($p = 0.000$). There was no significant effect on the PANA VIA™ V5 resin cement (10-MDP functional monomer) and the Super-Bond C&B resin cement (4-META functional monomer). That might be explained by their hydrophobicity compared to the NX3 Nexus™ resin cement (GPDM functional monomer).

The shear bond strength of our study was different from another study (81) after thermocycling 5,000 cycles. This study showed no difference in shear bond strength between etch-and-rinse mode and self-etched mode of the SBU/RU(TE) group and SBU/RU (SE) group ($p = 1.000$). These two groups were also different from group PV5 ($p = 0.038$, $p = 0.006$). While Guan and colleagues tested the micro-tensile bond strength after thermocycling 5,000 cycles, then reported that the micro-tensile bond strength of Single Bond Universal adhesive in etch-and-rinse mode was dropped significantly. On the contrary, the micro-tensile bond strength of the CLEAR FILL™ SE Bond, OptiBond™ XTR, and Single Bond Universal adhesive in the self-etched mode were not significantly different from the initial after 5,000 cycles (81). Another study investigated the effect of thermal aging on several resin cements to Zirconia restoration. There were several factors that affect the shear bond strength such as type of functional monomers, artificial aging time, crosshead speed (68), type of restorations, and other experimental designs.

The study of shear bond strength of different resin cements to zirconia restoration (83) found that the shear bond strength of PANA VIA™ V5 resin cement was dropped significantly after thermocycling 6,000 cycles, but the RelyX™ Ultimate™ resin cement had no significant changes in shear bond strength. The similar results were found in this study. The non-IDS PANA VIA™ V5 resin cement group had lower shear bond strength than the non-IDS RelyX™ Ultimate™ resin cement group. The possibility is that the RelyX™ Ultimate™ resin cement might be more hydrophobic when used along with the Single Bond Universal Adhesive compared with the PANA VIA™ V5 resin cement.

NX3 Nexus™ resin cement and Super-Bond C&B resin cement had low shear bond strength compared to other resin cement in this study. The GPDM-Ca complex and 4-MET-Ca complex on the dentin surface were not stable compared to the 10-MDP-Ca complex (30, 36).

In this study, when compared the shear bond strength of the MDP-based dental adhesives, whether universal adhesives, and other functional monomers found that the MDP-based functional monomers had high shear bond strength even there were no IDS. Meanwhile, the other functional monomers such as the GPDM required the IDS to gain the comparable shear bondable to the MDP-based dental adhesives. This might be the hydrophobic property of the polymerized MDP-based dental adhesives which can effectively bond to the hydrophobic resin cement. The GPDM-based dental adhesives, which is more hydrophilic, had higher shear bond strength when applied along with the IDS. This IDS layer might function as the hydrophobic layer to resist hydrolytic degradation. A 4-methacryloxyethyl trimellitic acid (4-META), the functional monomer of the Super-Bond C&B resin cement, was the carboxyl functional monomer. It has the carboxylic groups attached with the aromatic groups. The aromatic groups had the hydrophobic property which had the ability to buffer the acidity and to reduce the hydrophilicity of the carboxylic groups. 4-MET was the hydrolyzed 4-META. However, the chemical bond of 4-MET was still weaker compared to 10-MDP (30).

This study found that the shear bond strength of the SCB group was lower than the PV5 group significantly ($p = 0.017$). When dentin decalcification occurred, 4-META functional monomer in SCB group created 4-MET-Ca binding with hydroxyapatite that was a firmly chemical structure but lower than 10-MDP-Ca complex in PV5 group (36). The 10-MDP-Ca complex was more stable and harder dissolved than the 4 MET-Ca complex. This resulted in the bond durability of the hybrid layer in 10-MDP after water attacking this adhesive.

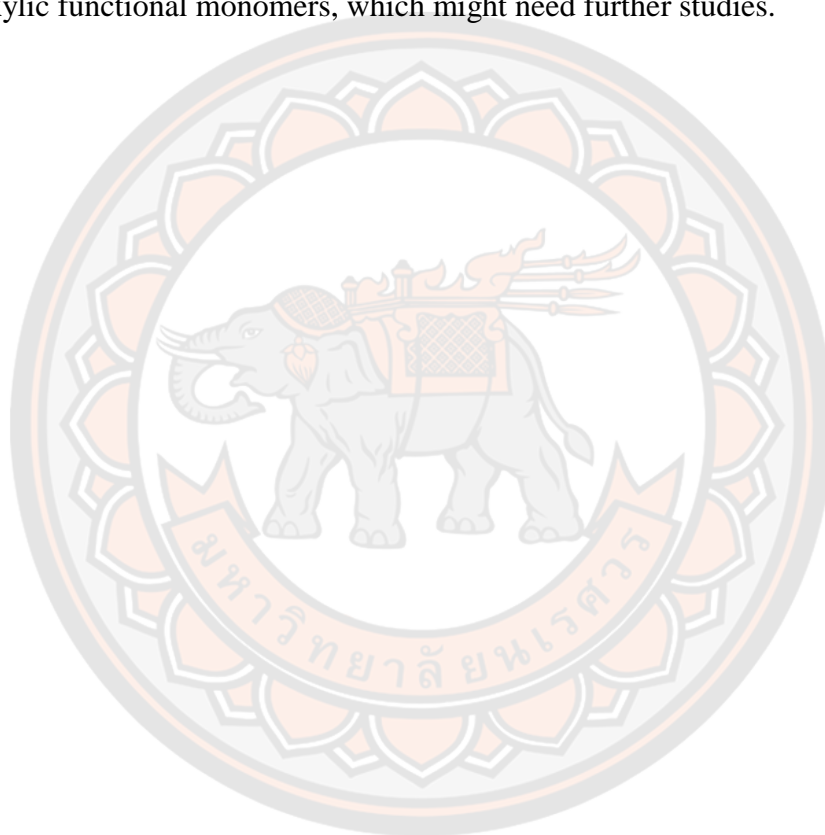
In the groups with the immediate dentin sealings similar composition of the dental adhesives (same company as the resin cement), the adhesive failure was predominant between the IDS and the adhesive of the resin cement. This might be resulting from the oxygen inhibiting layer removal. The oxygen inhibiting layer supports the adaptation of materials by decreasing the contact angle. This oxygen inhibiting layer allowed both materials bond to each other and copolymerization. This zone was called “the interdiffusion zone” (84). The maximum bond strength occurred as the wettability of the adhesion interface was properly maximized (85). Even the adhesive failures occurred at the IDS interface, they provide a higher shear bond strength than no IDS. Our result was similar to the failure mode of repairing composite as the most failure patterns occurred between aged-resin composite and the dental adhesive for new-resin composite (59, 86). Aged-resin composite had no unreacted monomers for the bond with other new resin composites. For improving the adhesion of repairing composite, the mechanical surface treatments such as sandblasting technique, grinding surface with a bur, and phosphoric etching of aged-resin composite promoted micromechanical retention of adhesion (59). On the contrary, our study using immediate dentin sealing with similar composition of the dental adhesives (same company as the resin cement) provided higher bond strength in NX3 Nexus™ resin cement.

In the different compositions of the dental adhesive groups (different company as the resin cement), the IDS with OptiBond™ XTR dental adhesive combined with PANA VIA™ V5 resin cement was insignificantly different on shear bond strength from either the PANA VIA™ V5 resin cement (no-IDS) or IDS with CLEARFIL™ SE BOND dental adhesive combined PANA VIA™ V5 resin cement (CSE-PV5 group). This same pattern was repeated in the results of the other three “different functional monomer” combinations. In each of these groups, the shear bond strength that resulted from combining the two different compositions of the dental adhesive was insignificantly different from either the baseline resin cement with the corresponding monomer or from the same functional combination with that similar composition of the dental adhesive of resin cement monomer.

The OXTR-PV5 group had higher shear bond strength comparable to the groups with the similar composition of IDS and the universal adhesive groups, even the majority of the failure mode was the adhesive failure between dentin and immediate dentin sealing. This might be the OXTR had hydrophilic property and low resistance to water from the dentinal tubules and thermocycles (87), but OXTR and PV5 were able to bind to each other with the phosphate functional molecules. The shear bond strength of the CSE-OXTR/NX3 group decreased compared to applying

IDS with a similar composition of the dental adhesive (SBU-SBU/RU(TE), SBU-SBU/RU(SE), and CSE-PV5), and the universal adhesive with no IDS. This might be more hydrophilicity of the OXTR while the polymerized CSE and NX3 were more hydrophobicity. The differences of the hydrophobicity might result in the different shear bond strength.

The shear bond strength of other different compositions (OXTR-SCB and CSE-SCB) significantly decreased compared to the groups with the Universal Adhesive with IDS (SBU-SBU/RU(TE) and SBU-SBU/RU(SE)), the universal adhesive with no IDS (SBU/RU(TE), and SBU/RU(SE)) and the 10-MDP IDS group (CSE-PV5). This might be the incompatibility between the phosphate and the carboxylic functional monomers, which might need further studies.



Conclusion

Similar-composition IDS with the resin cement adhesive could increase the shear bond strength of the restorations such as the OXTR-OXTR/NX3 group as different-composition IDS with the resin cement adhesive are insignificant differences in shear bond strength. However, when applying the universal adhesive together with RelyX™ Ultimate™ resin cement, provide the comparable shear bond strength without the immediate dentin sealing.



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