Bond strengths of three-step etch-and-rinse adhesives to silane contaminated dentin

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This study aimed to evaluate the effect of silane coupling agent contamination on the microtensile bond strength (μTBS) of 3-step etch-and-rinse adhesives on dentin. Flat occlusal dentin surfaces were prepared and randomly divided into 8 groups (n=20) based on the tested adhesives; Scotchbond Multi-purpose or Optibond FL, with contamination of an experimental silane (2 vol% of 3-m ethacryloxypropyltrimethoxysilane at pH 4.5) before acid-etching, after-etching or after-priming; while the groups without silane contamination served as controls. μTBS data were analyzed by two-way ANOVA and Tukey’s HSD tests at a significance level of 0.05. Additional specimens of contaminated dentin were used to analyze changes in the organic molecules by Fourier transform infrared spectroscopy (FTIR). Silane contamination before acid-etching did not significantly change μTBS (p>0.05), but contamination after-etching and after-priming significantly decreased μTBS of both adhesives (p<0.05). Silane contamination had an adverse effect on the dentin bond strength of 3-step etch-and-rinse adhesives especially after-priming.

Keywords: 3-step etch-and-rinse adhesive, Silane coupling agent, Microtensile bond strength, Contamination, Ceramic repairing

INTRODUCTION

Esthetic metal-free restorations have become increasingly popular in clinical practice, because of not only patients’ desires for esthetic restorations, but also the progressive developments in the mechanical properties and fabrication technologies of these materials. Glass ceramic or silica-based ceramic materials can be highly esthetic and possess sufficient strength for use as inlay, onlay, crown, or veneer restorations.

However, in clinical practice, complications; such as secondary caries, cervical abrasion and restoration fracture can occur1,4, in which either replacement or repair is chosen to resolve such problems. Many advantages of repairing rather than replacing a restoration, can be summarized as follows: preservation of tooth structure, a reduction in harmful effects on the dental pulp, reduced damage to adjacent teeth, reduced treatment times and costs, and good patient acceptance5). One strategy is to repair with resin composite or rebond the fractured part, which can be done intraorally using the appropriate bonding procedure6,7).

When repair-bonding to silica-based ceramic materials, the application of a silane coupling agent is recommended to promote chemical adhesion between silica particles and resin6,9). Silanes are composed of two reactive functional groups; alkxy functional groups, which are activated by hydrolysis before reaction with the surface hydroxyl groups of the inorganic substrate and organo-functional groups, which can react with organic resin monomers10,11). Furthermore, silane can increase the surface energy of the material to enhance resin wettability12,13). Therefore, silane application is an essential step to improve the bonding performance by chemical bonding between the silica-based ceramic and resin adhesive.

In case of intraoral repairs at the margins of ceramic restorations, two or more adhesive substrates including dentin or enamel, would be involved. These adhesive substrates require different adhesive treatments, in which there are risks of cross-contamination by silane from the adjacent adhesive substrate. A previous study has demonstrated that silane contamination on dentin prior to universal adhesive application either in etch-and-rinse or self-etch mode did not affect the dentin bond strength5). However, long-term bonding performance of universal adhesive is still insufficiently proven. Based on evidence of successful laboratory and long-term clinical performance, 3-step etch-and-rinse adhesive has been recommended for bonding to tooth substrates14). According to the 3-step etch-and-rinse adhesive protocol, phosphoric acid etching, priming and bonding procedures should be performed on tooth substrates without any contamination. Etching the dentin surface completely removes the smear layer and exposes the demineralized collagen fibril network, where resin monomers in
the primer and bonding agent can penetrate into
demineralized dentin and establish micromechanical
interlocking between the resin adhesive and dentin\textsuperscript{15}. It
should be noted that treatment of the exposed collagen
fibril network is the most critical factor for etch-and-
rinse systems to exhibit higher bonding performance.
Generally, a silane coupling agent contains ethanol as a
solvent as well as silane. Therefore, contamination of the
dentin surface during bonding procedures could affect the
expansion/shrinkage aspect of the exposed-collagen fibril
network\textsuperscript{16}, and might disrupt the monomer penetrating
process and influence resin-dentin bond strengths. Also,
the sequence of contamination; before etching, after
etching, or after priming might have different affects on
resin-dentin bond strengths. Unfortunately, information
on the effect of contamination of silane coupling agent
on the dentin bond strength of 3-step etch-and-rinse
adhesives is scarce.

Therefore, the purpose of this study was to evaluate
the effect of silane coupling agent contamination
during 3-step etch-and-rinse adhesives procedure on
microtensile bond strength to dentin. The null hypothesis
of this study was silane coupling agent contamination
has no adverse effect on the bond strength of 3-step etch-
and-rinse adhesives.

MATERIALS AND METHODS

Silane coupling agent preparation
A silane coupling agent was prepared by mixing
methacryloxypropyl trimethoxy silane (MPS; Merck,
Darmstadt, Hesse, Germany) with 70 vol\% ethanol
solution (mixture of 99.9 vol\% ethanol and deionized
water) to obtain 2 vol\% silane solution in accordance with
that published in study\textsuperscript{17}. 99.8% acetic acid was used to
adjust the pH to 4.5 to control the rate of hydrolysis of
MPS.

Specimen preparation
One hundred and sixty human caries-free permanent
third molars were used in this study after approval
by the Faculty of Dentistry Human Experimentation
Committee, Chiang Mai University No. 2/2018. Teeth
were stored at a temperature of \(-4\degree C\) and used within
1 month of extraction. The occlusal enamel was cut to
expose dentin and the teeth were ground with 600-grit
silicon carbide paper to create standardized smear layers.
The teeth were randomly divided into 8 groups based
on two commercial 3-step etch-and-rinse adhesives;
Scotchbond Multi-purpose (3M, St. Paul, MN, USA) or
Optibond FL (Kerr, Orange, CA, USA), with and without
contamination procedures of an experimental silane
before acid-etching, after acid etching or after priming
(Fig. 1). The experimental silane coupling agent and the
adhesives used are shown in Table 1. The adhesives were
applied to the dentin surface according to manufacturers’
instructions using a dry bonding technique.

Resin composite (Filtek Z350XT, 3M) was then
placed in 3 increments of 1.5 mm, each of which was
light-cured at the light intensity of 1,100 mW/cm\(^2\)±10%
for 20 s (Bluephase Style, Ivoclar Vivadent, Schaan,
Liechtenstein). The teeth were stored in distilled water
at 37\degree C for 24 h and then sectioned perpendicular to
the adhesive interface using a low-speed diamond saw
(IsoMet low speed cutter, Buehler, Lake Bluff, IL, USA)
under water cooling to obtain beam-shaped specimens
from each tooth at the resin-dentin interface with a
cross-sectional area of 1.0 mm\(^2\) (n=20).

Microtensile bond strength (\(\mu\)TBS) test
The beams were attached to a universal testing
machine (Instron 5566, Instron, Bangkok, Thailand)
with cyanoacrylate glue (Model repair II blue, Dentsply
Sirona, York, PA, USA) for the \(\mu\)TBS test at a crosshead
speed of 1 mm/min. The \(\mu\)TBS data were analyzed with
SPSS 22.0 (SPSS, Chicago, IL, USA), using two-way
ANOVA and Tukey’s HSD tests at significance level of
0.05.

Failure mode analysis
After testing to failure, all the specimens were sputter-
coated with gold (SPI-Module Sputter Coater, SPI
supplies, West Chester, PA, USA) and examined using a
scanning electron microscope (SEM; JSM-5910LV, JEOL,

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Fig. 1  Schematic representation of the experimental design.
Table 1  Materials used in this study

| Name [Batch number] | Composition | Application |
|---------------------|-------------|-------------|
| Scotchbond Multi-purpose (3M, St. Paul, MN, USA) [N731151] | Etchant: 35% H₃PO₄, silica thickener | Apply 15 s, rinse 20 s and air dry 5 s |
| | Primer: HEMA, polyalkenoic acid polymer, water, ethanol | Apply 15 s and air dry 5 s |
| | Adhesive: Bis-GMA, HEMA, tertiary amines, CQ, hexafluorophosphate, EDMAB, DHEPT | Air dry and light cure 10 s |
| Optibond FL (Kerr, Orange, CA, USA) [6502640] | Etchant: 37.5% H₃PO₄, water, silica thickener | Apply 15 s, rinse 20 s and air dry 5 s |
| | Primer: HEMA, GPDM, MMEP, water, ethanol, CQ, BHT | Actively rub 15 s and air dry 5 s |
| | Adhesive: Bis-GMA, HEMA, GDMA, CQ, ODMAB, filler (fumed SiO₂, barium aluminoborosilicate, Na₂SiF₆), coupling factor A174 | Actively rub, air dry and light cure 10 s |
| Experimental silane coupling agent (Merck, Darmstadt, Hesse, Germany) [K48642573 704] | Methacryloxypropyl trimethoxy silane (Silane A174), ethanol, acetic acid | Apply 60 s and air dry 5 s |

Bis-GMA: 2,2-bis[4-(2-hydroxy-3-methacryloxy-propoxy)-phenylene] propane; BHT: butylhydroxytoluene; CQ: camphorquinone; DHEPT: N,N-di-(2-hydroxyethyl)-4-toluidine (co-initiator); EDMAB: ethyl-4-(dimethylamino)benzoate; GDMA: glycerol dimethacrylate; GPDM: glycerol phosphate dimethacrylate; HEMA: 2-hydroxyethyl methacrylate; MMEP: mono-2-methacryloyloxyethyl phthalate; Na₂SiF₆: disodium hexafluorosilicate; ODMAB: 2-(ethylhexyl)-4-(dimethylamino)benzoate (co-initiator)

Tokyo, Japan). The fractured surfaces were classified into 4 categories18): 1. mixed failure (adhesive failure between dentin and resin, as well as cohesive failure within dentin and/or resin); 2. adhesive failure (failure between dentin and resin over 80% of the surface); 3. cohesive failure within dentin (failure in dentin over 80% of the surface); 4. cohesive failure within resin (failure in resin over 80% of the surface). The failure mode data were analyzed using the nonparametric Pearson Chi-square test.

Fourier transform infrared spectroscopy (FTIR)

Additional specimens for FTIR analysis were prepared in 5 conditions: acid-etched dentin with and without priming, silane contaminated dentin before and after etching and silane contaminated dentin after priming. A FTIR (Nicolet 6700 FT-IR Spectrometer, Thermo Fisher Scientific, Waltham, MA, USA) was used to take 64 scans at a resolution of 4 cm⁻¹ in the spectral range 4,000–400 cm⁻¹ to observe the composition change of collagen, resin monomer and silane on the dentin surfaces.

SEM observation

In order to observe the thickness of hybrid layer at resin-dentin interface, additional bonded specimens in each group were prepared as described above, where resin composite was built up in one 1.5-mm layer. After 24-h stored in distilled water, the specimens were sectioned parallelly to the interface using a low-speed diamond saw. The resin-dentin interface of each specimen was then polished using a sequence of 600-, 800-, 1000-, 1200-, 1500-, 2000-SiC papers. After being dehydrated and fixed in ascending grades of ethanol and hexamethyldisilazane (HMDS), respectively, the specimens were gold-sputter coated (SPI-Module Sputter Coater) and observed under a SEM (JEOL-5910LV) at 2,500× magnification.

RESULTS

µTBS test

The mean µTBSs of each group are shown in Table 2. The results of the two-way ANOVA revealed that the µTBS were significantly influenced by both factors: 3-step etch-and-rinse adhesives used (p<0.001) and silane contamination conditions (p<0.001). In addition, there was a significant interaction between the two factors (p<0.001).

The silane contamination before acid-etching did not significantly change µTBS (p>0.05). On the other hand, the contamination after etching significantly decreased the µTBS of both adhesives, and the contamination after priming caused a further significant reduction (p<0.001).

In each of the contamination conditions, Optibond FL adhesive showed significantly higher µTBS than Scotchbond Multi-purpose adhesive (p<0.001), except the silane contamination-after-priming groups (p=0.889).

Modes of failure

The results of the failure mode analysis from each group are summarized in Fig. 2. Most of failure modes
Fig. 2 Percentage of failure modes of the resin-dentin bond in each group (n=20).
The numbers in each bar are the number of fractional failure modes in each group.

Table 2 Mean and standard deviations of microtensile bond strength (MPa, n=20)

| Adhesive                  | Control group | Silane coupling agent contaminated groups |
|---------------------------|---------------|-------------------------------------------|
|                           | No contamination | Before etching | After etching | After priming |
| Scotchbond Multi-purpose  | 51.59 (4.68)   | 49.10 (5.29)  | 32.30 (4.92)  | 17.93 (4.68)  |
| Optibond FL               | 68.15 (6.85)   | 67.29 (6.05)  | 44.46 (4.79)  | 20.09 (3.33)  |

Groups identified by different superscript letter means a significant difference (p<0.05).

were adhesive failure, especially the groups, which were contaminated by the silane coupling agent after priming. There were significant differences in failure mode distribution among the groups (p<0.001).

**FTIR analysis**

The molecular changes, which occurred in each dentin condition are shown in Fig. 3. The FTIR spectra showed similar absorption bands around 1,633 cm⁻¹ (stretching vibrations of peptide C=O groups) and 1,544 cm⁻¹ (N–H bending vibrations coupled with C–N stretching vibrations) in all the dentin conditions, indicating amide I and amide II from collagen, respectively. In the primed acid-etched dentin and silane contamination-after-etching dentin, the absorption bands at 1,715 cm⁻¹ (carbonyl C=O stretching) and 810 cm⁻¹ (C=C twist), corresponding to monomers present in primer were observed.

An absorption band at around 476 cm⁻¹ (Si-O-Si) was observed in silane contamination-after-etching and after-priming dentin, which indicated residual silane on the dentin surfaces, but not in silane contamination-before-etching dentin.

**SEM observation**

Resin-dentin interfaces presenting the thickness of hybrid layer are shown in Fig. 4. In both of dental adhesives, silane contamination-after-priming groups (Figs. 4D and H) exhibited the thinner hybrid layers than the other groups.

Fig. 3 FTIR spectra of each dentin condition using (A) Scotchbond Multi-purpose, (B) Optibond FL.
**DISCUSSION**

The results of this study revealed that silane-contamination on dentin before the etching step did not change the dentin bond strengths of 3-step etch-and-rinse adhesives, but contamination after-etching and after-priming had a negative effect on dentin bond strengths. Therefore, the null hypothesis was partially rejected.

Generally, current commercial silane coupling agents contain 1–5 vol% MPS and ethanol in acidic condition. In this condition, the Si-O-CH₃ groups of MPS are hydrolyzed to silanol groups, which are responsible for chemically bonding to silica-based materials. However, the pre-hydrolyzed silane could have short shelf life, since the formation of Si-O-Si oligomers by self-condensation between silanol groups in the acidic condition decreases the activity of silane over time.

This study focused on the effect of residual products of MPS and ethanol on the dentin surface on dentin bonding. Thus, an experimental silane coupling agent was prepared by mixing MPS in the ethanol solution with acetic acid just before use in order to ensure hydrolysis to the silanol groups on the adhesive dentin surface.

In this study, the silane contamination-before-etching groups did not exhibit a significant alteration in µTBS from the non-contaminated groups. As with previous dentin bonding studies on the effects of contamination with blood and saliva, and pre-application with metal primer, the contaminants would be rinsed off with water from the dentin surface etched with phosphoric acid. It was confirmed by FTIR result, where the silane contamination-before-etching dentin showed the absorption bands without Si-O-Si peak, that was referred as acid-etch dentin. The absence of a Si-O-Si peak in the absorption band of 476 cm⁻¹ indicated that silane was washed away by phosphoric acid etching and water rinsing steps. Therefore, the bond strengths of silane contamination-before-etching groups were comparable to the control groups. However, this application procedure would not affect the silane-treated ceramic, because etching and water washing did not significantly improve or reduce the bond strengths of silane-treated ceramic.

Normally, air-blowing after phosphoric acid etching can shrink the exposed collagen fibril network on the dentin surface as a result of the rapid evaporation of water, and the surface tension forces operating at the air-water interface. These allowed interpeptide hydrogen bonds between adjacent collagen fibrils, resulting in the reduction of interfibrillar spaces for resin monomer penetration. Additionally, it was found that much of the bound water still remained in the intrafibrillar compartments of the collagen fibrils even if unbound or free water in interfibrillar compartments was evaporated by air-drying. This bound water could interfere with the infiltration of the dental adhesive into the intrafibrillar compartment of collagen fibrils, resulting in a reduction in bond strength. On the other hand, silane-contamination after acid-etching would allow the penetrating ethanol on the dentin surface to slightly re-expand the collagen fibril network, allowing the collagen fibril network to re-expand. Additionally, ethanol soaking could further remove some amounts of remaining water from the intrafibrillar compartment of the collagen molecules as well as the interfibrillar compartment. The penetrating ethanol might improve the permeation of primer components into the intrafibrillar compartment of the collagen molecules. Furthermore, it has been speculated that the MPS molecule (molecular weight=234 Da) dissolved in ethanol can also penetrate into the collagen fibrils, where the silanol group would then react with the hydroxyl groups of the fibrils by forming hydrogen bonds.

The subsequent application of a primer on silane-contaminated acid-etched dentin was expected to re-
expand the collapsed collagen fibril network. Previous research has demonstrated that a primer containing HEMA-water or HEMA-ethanol could re-expand the demineralized collagen matrix on dried dentin\(^\text{[}2\text{]}\). Furthermore, the primers used in this study contain a quantity of the acidic monomers; polyalkenoic acid copolymer in Scotchbond Multi-purpose and GPDM in Optibond FL, rendering these primers to be acidic. However, the results of this study showed that the µTBSs of the silane contamination-after-etching group were significantly lower than those of the non-contaminated control and silane contamination-before-etching groups. The unstable H-bond between MPS molecules and fibrils might be broken by following primer application, then the released MPS might undergo self-condensation, forming Si-O-Si oligomers\(^\text{[}3\text{]}\), or interacting with acidic monomers in the primer\(^\text{[}4\text{]}\). As evidenced in the FTIR spectra of the silane contamination-after-etching groups, Si-O-Si oligomers on the dentin surface at the absorption bands of 476 cm\(^{-1}\) were present. Although self-condensation requires a long time in acidic solution, reported to be 2 h in a pH of 2.7 in a previous study\(^\text{[}5\text{]}\), the relatively higher pH of the primer solution, or the higher concentration of MPS dissolved into the primer might enhance the condensation rate of MPS\(^\text{[}3\text{]}\). Otherwise, the free silanol groups may undergo self-condensation during solvent evaporation as evidenced by NMR research\(^\text{[}6\text{]}\).

It was speculated that the presence of Si-O-Si oligomers absorbed on dentin surface in the silane contamination-after-etching group hindered the hydrophilic character of the dentin surface, which is determined by surface –OH concentration, and instead showed hydrophobic characters on contaminated dentin\(^\text{[}6\text{]}\). Thus, the presence of Si-O-Si oligomers might interrupt the infiltration of hydrophilic monomers in the primer, resulting in a reduction of the bond strength to silane-contaminated etched dentin. The results of this study were contrary to the previous study, which demonstrated that silane contamination on dentin prior to universal adhesive application had no effect on dentin bond strength\(^\text{[}7\text{]}\). Although the silane contamination on acid-etched dentin in this study was comparable to the contamination in etch-and-rinse mode of universal adhesive, the successive applied agents were different. Universal adhesive is relatively more hydrophobic than primer of 3-step etch-and-rinse adhesive\(^\text{[}8\text{]}\). Therefore, the monomers might infiltrate contaminated dentin in different manner.

The contamination of silane coupling agent after priming revealed the lowest µTBS, and all the specimens debonded at the adhesive interface. These results would indicate inferior penetration of the adhesive monomer into etched dentin. It has been established that the priming step helps maintain the interfibrillar spaces within the collagen fibril network, as well as increasing surface energy\(^\text{[}9\text{]}\). Thus, the primed acid-etched dentin would be ready for the infiltration of relatively hydrophobic monomers\(^\text{[}10\text{]}\). Subsequent silane-contamination on the primed acid-etched dentin would disrupt those surface characteristics, since ethanol in the silane coupling agent would dissolve the primer components bound to the collagen fibril network into the solution again. Attempting to evaporate concentrated ethanol by air-drying, could further remove free monomers such as HEMA\(^\text{[}11\text{]}\), leaving a lesser amount of bound primer monomers on the dentin surface to maintain the collagen fibril network. As a result, air-drying after contamination of the silane coupling agent could cause re-collaps of the collagen fibril network\(^\text{[12,32]}\), leading to a lesser degree of interfibrillar spaces in the collagen fibril network\(^\text{[32,32]}\). This speculation was evident in SEM images of silane contamination-after-priming groups in both dental adhesives, whose hybrid layers were thinner than that of controls and the other contaminated groups. Furthermore, the application of silane coupling agent on the primed-dentin surface might create a new high concentration mixture of ethanol and monomers, which might reduce the vapor pressure of ethanol upon ethanol evaporation\(^\text{[13]}\). Thus, there is an increased possibility of residual ethanol being retained on the dentin surface, which could impair polymerization and weaken the strength of the adhesive layer\(^\text{[32]}\). Additionally, the MPS molecules undergo self-condensation when left on the primed acid-etched dentin surface, which could impair the penetration of adhesive monomers in the bonding agent. It is also speculated that the MPS molecules might copolymerize with resin monomers and this may worsen, as the incorporation of large molecules could increase resin viscosity and lower the degree of conversion\(^\text{[32]}\). These would be a reason why the µTBSs in the silane contamination-after-priming groups reduced and all the specimens showed adhesive failure.

Regarding the type of adhesive, Optibond FL showed significantly higher µTBS than Scotchbond Multi-purpose. In accordance with a previous study\(^\text{[44]}\), Scotchbond Multi-purpose contains polyalkenoic acid copolymer, which has high molecular weight and doesn’t dissolve in adhesive solution, causing phase separation and resin globules formation in a polymer that cannot penetrate into collagen fibril network. This polyalkenoic acid copolymer can be deposited as gel on the collagen surface\(^\text{[55,56]}\), and impede monomer infiltration\(^\text{[46]}\).

In this study, an experimental silane coupling agent was prepared in acidic form by mixing with acetic acid before use. One might argue that the acidic pH of the silane solution resulted in further demineralization of the dentin and lead to too deep a demineralized collagen matrix for complete monomer infiltration. However, a previous study revealed a protective effect for the demineralized organic matrix presenting on the lesion surface against the acid attack by interfering with the diffusion of ions outside and inside the demineralized area\(^\text{[57]}\). Thus, the effect of pH of the silane solution might be negligible. Within the limitations of this study, it was concluded that contamination of the silane coupling agent on dentin affected the dentin bond strength of the tested 3-step etch-and-rinse adhesives, which could be mainly attributed to the presence of residual MPS on the dentin surface after etching and priming as well as...
the effect of ethanol solvent in the exposed collagen fibril network.

In this study, the silane contamination after priming dramatically decreased dentin bonding of 3-step etch-and-rinse system. Therefore, when bonding of 3-step etch-and-rinse system to the surface combined with ceramic restorative materials and dentin surface, the silane contamination after priming should be strictly avoided. In addition, the results of this study indicated that silane coupling agent should be specifically applied on ceramic surface before primer application to dentin surface.

CONCLUSION

The silane contamination on dentin surface especially after priming step decreased the dentin bond strength of 3-step etch-and-rinse dental adhesive. Therefore, in intraoral repair of ceramic, silane coupling agent should be applied on ceramic before primer application on dentin.

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