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# Effect of Silane Coupling Agent on the Shear Bond Strength Between Lithium Disilicate Glass Ceramic and Composite Resin

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## Abstract

**Objectives:** To evaluate the shear bond strength of various concentrations of silane coupling agents between lithium disilicate glass (LDS) ceramic and composite resin.

**Methods:** Seven groups ($n$=7) of experimental silane coupling (ESC) agent, including 1%, 3%, 6%, 9%, and 12% (v/v) concentrations, were prepared for silanization and non-silanization (NS) and commercial silane coupling (CSC) agent groups served as controls. The shelf life of ESCs was evaluated at 0, 1, 2, 4, 8, 16, and 32 days after hydrolysis. Shear bond strength test was performed. The mode of failure, fracture surface topography, and elemental analysis were evaluated.

**Results:** The mean shear bond strength of NS, CSC, and ESC groups in non-thermocycling and thermocycling ranged from 7.3 to 26.3 and 1.8 to 18.2 MPa, respectively. The results were statistically analyzed using Two-way ANOVA, followed by Tukey's multiple comparison test ($\alpha$=0.05). These results showed that the shear bond strength of the NS group (1.8 MPa) after thermocycling was significantly lower than that of the ESC and CSC groups, while the 6% ESC group (18.2 MPa) showed a higher shear bond strength than the other groups. The mean shear bond strengths after 0, 1, 2, 4, 8, 16, and 32 days of hydrolyzing 6% ESC ranged from 13.7 to 18.2 MPa.

**Conclusions:** The 6% ESC group had the highest shear bond strength. The shear bond strength decreased significantly after the thermocycling. The shear bond strength of the hydrolyzed silane coupling agent gradually decreased after being hydrolyzed over time after hydrolysis.

**Keywords:** composite resin, lithium disilicate glass ceramic, shear bond strength, silane coupling agent, silanization

## Introduction

Ceramic restorations were introduced in the 1980s[(1)], and thereafter, they have been widely used in dentistry owing to their natural appearance, chemical stability, biocompatibility[(2)], high compressive strength, and a coefficient of thermal expansion similar to that of the tooth structure.[(3)] The esthetic appearance of all ceramic restorations is superior than that of porcelain-fused-to-metal restorations.[(4)] The mechanical properties of lithium disilicate glass ceramic (LDS), which is a second-generation silica-based ceramic, are better than those of the first-generation silica-based ceramics. Furthermore, LDS is highly translucent and can mimic natural tooth colors. Therefore, they are considered as the most promising alternatives for restoring tooth structure.

The clinical success rate of all ceramic restorations depends on the quality of cementation.[5] In cementation, the bond between the ceramic restoration and tooth structure consists of two parts: the tooth surface-adhesive agent and the adhesive agent-ceramic surface. The shear bond strength between the adhesive agent and the ceramic surface plays a crucial role in clinical success.[3]

Ceramic surface treatments can be divided into mechanical and chemical surface treatments.[6] Mechanical surface treatments, such as sandblasting and chemical etching, can create micromechanical retention on the ceramic surface, which leads to bonding with the adhesive agents.[7,8] However, sandblast surface treatment is not recommended due to the insufficient bond strength with silica-based ceramics.[3,5] Chemical surface treatment involves etching with hydrofluoric acid (HF) at various concentrations between 8 and 10% for 2 to 2.5 min depending on the manufacturer's instructions. The micromorphologic change after HF etching can create a honeycomb-like topography on the ceramic surface, resulting in micromechanical retention.[3,8] Chemical surface treatment also involves the application of a silane coupling agent, which is a major bonding agent, that provides a chemical bond to silica-based ceramics.[7] Therefore, the recommended surface treatment to achieve high bond strength is HF etching, which performs micromechanical retention, as well as silane coupling agent that produces the chemical bond.[3,9]

Silane coupling agent is a bifunctional molecule that acts as an adhesive agent between the inorganic particles, i.e., silicon oxide on the ceramic surface, and the organic substance of the adhesive agent matrix. The silane coupling agent widely used in dentistry is γ-methacryloyloxypropyltrimethoxysilane (MPS).[10] It has short chain and low molecular weight molecules that can minimize the homocondensation of MPS.[7] In addition, it has a minimal color effect from its refractive index (1.43)[11], which is similar to that of the ceramic materials (1.45).[12] In previous studies, different concentrations of silane coupling agents have been varied between 1 and 10% (v/v).[10,13] The 5% (v/v) MPS provided the highest shear bond strength after treatment with glass or resin materials[14], whereas that between polymethylmethacrylate (PMMA) and alumina plate that were silanized with 1% (v/v) MPS in 70% (v/v) ethanol resulted in a statistically significant shear bond strength.[15] However, the appropriate concentration of the silane coupling agent on the shear bond strength between the ceramic and composite resin remains controversial.

The effects of the silane coupling agent depend on the silane concentration, solution, temperature, and shelf life.[16] The shelf life of the hydrolyzed silane coupling agent is an important factor affecting the shear bond strength. After the silane coupling agent was hydrolyzed, it changed to an active form (hydrolyzed silane coupling agent) and tended to undergo homocondensation. In homocondensation, the silane coupling agent can react with the silica surface; however, the quality of the bond strength is unpredictable.[17] Previous studies on the shelf life of silane coupling agents after hydrolysis were inconclusive.

Therefore, this study aims to investigate the shear bond strength of various concentrations of experimental silane coupling agent (ESC) between LDS and composite resin under non-thermocycling and thermocycling conditions, as well as the effect of the shelf life of the hydrolyzed silane coupling agent on the shear bond strength between LDS and composite resin. The null hypotheses were that there would be no significant differences in the shear bond strength between LDS and composite resin with various concentrations of silane coupling agent and thermocycling challenge. There would be no significant differences in the shear bond strength between LDS and composite resin after 0, 1, 2, 4, 8, 16, and 32 days of hydrolysis of the silane coupling agent.

## Materials and Methods

### *Silane coupling agent and solutions*

The silane coupling agent, solutions, ceramic, and materials used and their manufacturers are listed in Table 1. The chemicals were used as received.

### *Preparation of specimens*

The LDS specimens (IPS e.max Press, Ivoclar Vivadent, Schaan, Leichtenstein) were prepared by the lost-wax technique and cut into cylindrical shape (13.0 mm in diameter and 2.0 mm in thickness) using a low-speed diamond saw (Isomet® 5000, Buehler Ltd., IL, USA) with a speed of 1,500 rpm and feed rate of 1.5 mm/min. The surface of the LDS specimen was observed under six magnifications using a stereomicroscope

**Table 1:** The silane coupling agent, solutions, ceramic, and materials used in the present study and their manufacturers.

| Materials | Concentrations (%(v/v)) | Code | Brand | Manufacturer | Batch No. |
|---|---|---|---|---|---|
| ***Silane coupling agent*** | | | | | |
| ɤ-methacryloxy propyltrimethoxysilane | 98.0 | MPS | Sigma-Aldrich® | Sigma- Aldrich® Pte Ltd., Mo, USA | SHBK 9588 |
| ***Solutions*** | | | | | |
| Ethanol | 99.9 | ETH | RCI Labscan | RCI Labscan Ltd., Bangkok, Thailand | 19110052 |
| Tetrahydrofuran | 99.8 | THF | RCI Labscan | RCI Labscan Ltd., Bangkok, Thailand | 19120112 |
| ***Ceramic*** | | | | | |
| Lithium disilicate glass ceramic | | LDS | IPS e.max Press | Ivoclar Vivadent, Schaan, Liechtenstein | YY25357 |
| ***Materials*** | | | | | |
| Commercial silane coupling agent | | CSC | Porcelain liner M | Sun Medical Company, Ltd., Shiga, Japan | SF1 |
| Adhesive agent | | A | Single Bond Universal adhesive | 3M™ ESPE, MN, USA | 881130A |
| Hydrofluoric acid | 9 | HF | Porcelain Etch | Ultradent Products | BKCWM |
| Flowable composite resin | | | Filtek™ Supreme Flowable restorative | Inc, UT, USA 3M™ ESPE, MN, USA | NC9309 |

(Olympus SZX2-ILLT, Olympus Corporation, Tokyo, Japan) to determine the cracks on the surface of the LDS specimens. The cracked specimens were then excluded.

Herein, 158 LDS specimens were placed into a cylindrical polyvinylchloride mold (20.0 in diameter and 15.0 mm in thickness) and fixed with autopolymerized acrylic resin (Fast Curing Custom Tray Acrylic Resin; Instant Tray Mix, Lang dental manufacturing company, IL, USA). The LDS specimens were polished with wet silicon carbide papers #800, #1000, and #1200 using a polishing machine (Twin variable-speed grinder polisher Phönix Beta 601990, Buehler Ltd., IL, USA). The cracked surface of the LDS specimens was determined after polishing using a stereomicroscope and cleansing using an ultrasonic cleaner device (SONOREX SUPER 10 P DK 255 P, BANDELIN electronic GmbH & Co. KG, Berlin, Germany) for 5 min.

After polishing with wet silicon carbide papers, the surface roughness (*Ra*) was measured using an atomic force microscope (Nanosurf C3000, Nanosurf Inc., Liestal, Switzerland) and calculated using software (C3000 Control Software Version 3.5, Nanosurf Inc., Liestal, Switzerland). In all the groups, the *Ra* values were calculated using One-way analysis of variance (ANOVA). The insignificant differences in the *Ra* values in all the groups were considered into the experimental specimens. The surface treatment area of the LDS specimen surface was located at the center of the specimen with a diameter of 5.0 mm.

The LDS specimens were divided into 3 parts as follows:

### *Part I: The various concentrations of ESC and thermocycling conditions*

Herein, 98 LDS specimens were randomly divided into two conditions: non-thermocycling and thermocycling. Each condition group was divided into seven groups ($n$=7), i.e., 5 groups of various concentrations of ESC, including 1%, 3%, 6%, 9%, and 12% (v/v), and two control groups, which were non-silanization (NS) and commercial silane coupling agent (CSC). The varying concentrations of ESC were prepared by the silanization process as follows.

### *Silanization process*

The ethanol (99.9% (v/v)) (ETH; RCI Labscan Ltd, Bangkok, Thailand) was diluted to 70% ETH with deionized water at room temperature (RT) (23±2°C). The mentioned concentrations of ESC were prepared by mixing γ-methacryloxypropyltrimethoxysilane (Sigma-Aldrich® Pte Ltd., Mo, USA) with ETH. The reagents were hydrolyzed using a magnetic stirrer (OkWell 6 Ch Stirrer, Progress Technical Co., Ltd., Bangkok, Thailand) for 5 min.

### *Surface treatment*

*1. Hydrofluoric acid*

The surface of the LDS specimen was conditioned with 9% HF (Ultradent® Porcelain Etch, Ultradent Products Inc., UT, USA) for 90 s in accordance with the manufacturer's instructions. The LDS specimens were rinsed with deionized water for 15 s and dried with an air blow using a triple syringe.

*2. Experimental silane coupling agent*

Thereafter, 50 $\mu$L of each concentration of silane coupling agent was applied to the bonding area of the LDS specimens using a micropipette (Pipetman® Classic, Gilson Inc., Middleton, USA) and dried at RT for 1 min.

*3. Commercial silane coupling agent*

Porcelain liner M (prehydrolyzed silane coupling agent; Sun Medical Company Ltd., Shiga, Japan) was used as a CSC agent. Herein, 14 LDS specimens from the CSC group were treated with Porcelain liner M in accordance with the manufacturer's instructions.

### *Adhesive agent*

The adhesive agent (Single Bond Universal adhesive, 3M ESPE, MN, USA) was applied to the bonding area of the LDS specimens and dried to create a thin film of adhesive layer. The adhesive layer was cured with an LED light-curing unit (Elipar™ S10 LED Curing Light; intensity 1,200 mW/cm$^2$, 3M ESPE, MN, USA) for 10 s in accordance with the manufacturer's instructions.

### *Composite resin*

The flowable composite resin (Filtek™ Supreme Flowable restorative, 3M ESPE, MN, USA) was injected into a polyvinylchloride mold (5.0 mm in diameter and 3.0 mm in height) over the surface treatment area, covered with celluloid strip, and then light activated on each side with five overlapping for 20 s each using LED light-curing unit for 20 s.

### *Thermocycling challenge*

All the LDS specimens were stored in a dry electronic cabinet (EuRaKa Dry Tech DX-126 Auto Dry Box, Taiwan Dry Tech Corporation, Taipei City, Taiwan) at 37°C for 24 h. Seven LDS specimens in each group were randomly selected for thermocycling conditions. Thermocycling was performed by immersing the specimens in 5°C and 55°C deionized water for 30 s for 5,000 cycles of dwelling time[18,19] using a thermocycling machine (Thermocycler THE 1200, SD Mechatronik GmbH, Bavaria, Germany).

### *Shear bond strength test*

The shear bond strength test was performed using a universal testing machine (ElectroPlus™ E1000, Instron®, MA, USA) at a crossed-head speed of 0.5 mm/min. The specimens were fixed on a shear bond jig to locate a chisel-shaped rod of the load cell parallel to the bonding interface (Figure 1). The shear bond strength was calculated using software (Bluehill® Universal Materials Testing Software, Instron®, MN, US) with the following equation:

$$\tau = F/A \ (N/mm^2),$$

*where* $\tau$ is the shear stress ($N/mm^2$), F is the applied force ($N$), and $A$ is the cross-sectional area of the material with area parallel to the applied force vector (mm$^2$).

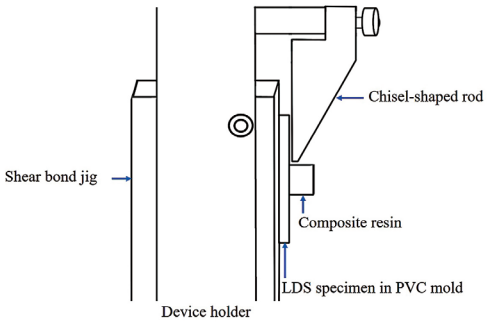


**Figure1:** Schematic diagram showing setup of the LDS specimens for shear bond test.

### *Mode of failure analysis*

The fracture surface characteristics of all experimental LDS specimens after shear bond strength test in part I were examined under six magnification of stereomicroscope. The mode of failures of all experimental LDS specimens in non-thermocycling and thermocycling conditions were categorized into 3 characteristics; adhesive failure, cohesive failure, and mixed failure mode. According to the LDS specimens in the adhesive and mixed failure mode, the composite resin remnants were recorded using Image J software (Image J 1.53k, National Institutes of Health (NIH), Maryland, USA). The mean percentage composite resin remnants were calculated as follows:

$$\text{The mean percentage composite resin remnants} = \frac{\text{The composite resin remnants}}{\text{The total bonding area of LDS specimens}} \text{ X 100}$$

### *Scanning electron microscopy (SEM)*

The fractured surfaces of the LDS specimens after the shear bond strength tests were observed using an SEM (Leo 1455VP, Carl Zeiss Microscopy GmbH, Jena, Germany). After the shear bond strength test, the fractured surfaces of the LDS specimens were coated with a thin layer of gold. The primary electron beam energy was operated at 20 keV for each specimen.

### *Part II: Shelf life of hydrolyzed silane coupling agent*

Based on the shear bond strength test results in *Part I*, 6% ESC group showed the highest shear bond strength and was therefore selected to evaluate the shelf life of the hydrolyzed silane coupling agent.

Herein, 49 LDS specimens were divided into seven groups ($n$=7) at 0, 1, 2, 4, 8, 16, and 32 days after the silanization process. The procedures of the LDS specimen preparation, silanization process, adhesive agent, composite resin, thermocycling condition, and shear bond strength test were similar to those of *Part I*.

### *Part III: Elemental analysis*

To clarify the effectiveness of silane coupling agent deposition on the LDS surface after silanization, the LDS specimens were washed with an excess silane coupling agent with tetrahydrofuran (THF; RCI Labscan Ltd., Bangkok, Thailand).

Eleven LDS specimens were prepared for the silanization process with 1%, 3%, 6%, 9%, and 12% ESC groups following the above-mentioned procedures. In each ESC group, the specimens were divided into two conditions: washed THF and unwashed THF.

In the washed THF condition, the homocondensation and physisorbed layers of the silane coupling agent were removed.[20,21] The washing procedure was repeated until the THF supernatant showed only an absorbance peak at 250 nm using a spectrophotometer (SpectraMax® M3 Microplate Reader, Molecular Devices LLC, California, USA). This procedure indicated that it was possible to completely remove the homocondensation and physisorbed layer from the surface of the LDS specimen.

Energy dispersive X-ray spectroscopy (EDS; S-3400N-II, Hitachi High-Technologies Corporation, Tokyo, Japan) was used to evaluate the qualitative and quantitative characteristics of the elements on the surface of the specimens. A thin layer of gold was coated onto the surface of the LDS specimens. The primary electron beam energy was operated at 20 keV for each specimen. Three areas of 0.25×0.18 mm, which were the center of the specimen, were examined. The non-silanized surface of the LDS specimen was treated with 9% HF and analyzed as a reference (Etched LDS group). EDS analysis can detect carbon (C), oxygen (O), and silicon (Si) atoms on the silanized LDS surface. Si and O atoms can be detected on the non-silanized and silanized surfaces of the LDS specimens. Therefore, the C atom is the appropriate element to demonstrate that the silane coupling agent reacted on the LDS surface.

### *Statistical analysis*

The shear bond strength of various concentrations of the silane coupling agent under non-thermocycling and thermocycling conditions was analyzed using Two-

way ANOVA, followed by Tukey's *post-hoc* comparison (SPSS version 20, IBM, Armonk, NY, USA). The shear bond strength of various concentrations and shelf life of the hydrolyzed silane were determined using One-way ANOVA and Tukey's *post-hoc* comparison. The significance level was set at α=0.05.

## Results

### *Part I: The various concentrations of ESC and thermocycling conditions*

Two-way ANOVA showed that the interaction of the two main factors between the silane coupling agent concentrations and the thermocycling challenge was insignificant. Nevertheless, the effect of each factor was statistically significant among the groups. Therefore, One-way ANOVA and Tukey's HSD tests were performed to compare all the conditions. The means and standard deviations of the shear bond strength under non-thermocycling and thermocycling conditions are shown in Table 2.

The means of the shear bond strength of the NS, CSC, and 1%, 3%, 6%, 9%, and 12% ESC groups with non-thermocycling conditions ranged from 7.3 to 26.3 MPa. One-way ANOVA revealed significant differences between the groups. Tukey's HSD indicated that the means of the shear bond strength of 3%, 6%, 9%, and 12% ESC groups were 23.2, 26.3, 22.8, and 22.1 MPa, respectively, all of which were significantly higher than those of the other groups. The 6% ESC group exhibited the highest shear bond strength. Furthermore, the mean shear bond strength of the NS group was 7.3 MPa, and it revealed significantly lower shear bond strength than that of the CSC and ESC groups.

Under thermocycling conditions, the means of the shear bond strength of the NS, CSC, and 1%, 3%, 6%, 9%, and 12% ESC groups ranged from 1.8 to 18.2 MPa. One-way ANOVA revealed significant differences between the groups. Tukey's HSD indicated that the shear bond strengths of 3%, 6%, and 9% were 15.6, 18.2, and 15.9 MPa, respectively, which were significantly higher than those of the other groups. The 6% ESC group exhibited the highest shear bond strength. The mean shear bond strength of the NS group was 1.8 MPa, which was significantly lower than that of the CSC and ESC groups. Consequently, Two-way ANOVA revealed significant differences between the groups in the non-thermocycling and thermocycling conditions. In other words, the shear bond strength in the non-thermocycling conditions was significantly higher than that in the thermocycling conditions.

After the shear bond strength test, all experimental LDS specimens in *Part I* were observed under six magnifications using a stereomicroscope to determine the mode of failure. The mode of failure of the experimental LDS specimens under non-thermocycling and thermocycling conditions is shown in Table 3. The mean percentages of composite resin remnants in the 6% ESC group with non-thermocycling and thermocycling conditions were 30.8% and 8.9%, respectively.

**Table 2:** The means and standard deviations of shear bond strength in non-thermocycling and thermocycling conditions.

| Surface treatment (%(v/v)) | Shear bond strength (MPa) | |
|---|---|---|
| | Non-thermocycling | Thermocycling |
| NS | 7.3 (1.0)$^{d}$ | 1.8 (0.6)$^{D}$ |
| CSC | 18.0 (2.3)$^{c}$ | 13.8 (2.0)$^{B,C}$ |
| 1% ESC | 20.5 (4.5)$^{b,c}$ | 14.5 (2.3)$^{B,C}$ |
| 3% ESC | 23.2 (2.7)$^{a,b}$ | 15.6 (2.3)$^{A,B}$ |
| 6% ESC | 26.3 (2.6)$^{a}$ | 18.2 (1.8)$^{A}$ |
| 9% ESC | 22.8 (3.3)$^{a,b,c}$ | 15.9 (2.3)$^{A,B}$ |
| 12% ESC | 22.1 (3.4)$^{a,b,c}$ | 12.0 (3.0)$^{C}$ |

Mean values ($n$=7) and standard deviations in parentheses.
NS=Non-silanization
CSC=Commercial silane coupling agent
ESC=Experimental silane coupling agent
*Superscript lowercase letters denoted with same letter are not significantly different ($p$>0.05).
*Superscript capital letters denoted with same letter are not significantly different ($p$>0.05).

**Table 3:** Mode of failures and means percentage of composite resin remnants of experimental LDS specimens in non-thermocycling and thermocycling conditions ($n$=7).

| Surface treatment | Mode of failures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Non-thermocycling | | | | Themocycling | | | |
| | Adhesive n | Cohesive n | Mixed n | Means of composite resin remnants (%) | Adhesive n | Cohesive n | Mixed n | Means of composite resin remnants (%) |
| NS | 7 | 0 | 0 | 0 | 7 | 0 | 0 | 0 |
| CSC | 6 | 0 | 1 | 12.9 | 5 | 0 | 2 | 4.9 |
| 1% ESC | 3 | 0 | 4 | 13.5 | 3 | 0 | 4 | 5.0 |
| 3% ESC | 2 | 0 | 5 | 26.5 | 3 | 0 | 4 | 5.1 |
| 6% ESC | 0 | 0 | 7 | 30.8 | 0 | 0 | 7 | 8.9 |
| 9% ESC | 2 | 0 | 5 | 14.7 | 3 | 0 | 4 | 2.0 |
| 12% ESC | 4 | 0 | 3 | 10.0 | 5 | 0 | 2 | 1.9 |

NS=Non-silanization
CSC=Commercial silane coupling agent
ESC=Experimental silane coupling agent

### *Part II: Shelf life of hydrolyzed silane coupling agent*

The means and standard deviations of the shear bond strength values of 0, 1, 2, 4, 8, 16, and 32 days after hydrolyzing 6% ESC are summarized in Table 4. The values ranged from 13.7 to 18.2 MPa. One-way ANOVA revealed significant differences between groups. The means of the shear bond strength at 0 and 1 day after hydrolyzing the 6% ESC group were 18.2 MPa and Tukey's HSD was significantly higher than those of the other groups. Moreover, the shear bond strength of the hydrolyzed 6% ESC gradually decreased over time. The shear bond strength at 32 days after hydrolyzing the 6% ESC group was 13.7 MPa, which was significantly lower than that of the other groups.

**Table 4:** The means and standard deviations of the shear bond strength of hydrolyzed 6% ESC.

| Day | Shear bond strength (MPa) |
|---|---|
| 0 | 18.2 (1.8)$^{A}$ |
| 1 | 18.2 (2.3)$^{A}$ |
| 2 | 17.1 (2.8)$^{A,B}$ |
| 4 | 16.4 (2.6)$^{A,B}$ |
| 8 | 14.6 (1.6)$^{A,B}$ |
| 16 | 14.6 (1.6)$^{A,B}$ |
| 32 | 13.7 (2.5)$^{B}$ |

Mean values ($n$=7) and standard deviations in parentheses.
*Superscript letters denoted with same letter are not significantly different ($p$>0.05).

### *Part III: Elemental analysis*

The atomic percentages of C atoms on the surface of the LDS specimens in unwashed THF and washed THF conditions are shown in Figure 2. After silanization in the unwashed THF condition, the atomic percentage of C atoms ranged from 0.08 to 7.41. The atomic percentage of C atoms gradually increased and reached the highest value in the 12% ESC group. The atomic percentage of C atoms after THF washing ranged from 1.38 to 2.88 and gradually increased from 1% in the ESC group and reached a plateau in the 6% ESC group.

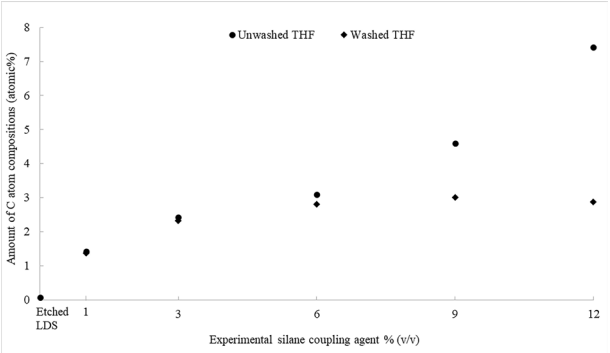


**Figure 2:** The atomic percentages of carbon (C) atom on the surface of LDS specimens in unwashed tetrahydrofuran (THF) and washed THF conditions.

## Discussion

This study evaluated the effect of different concentrations of silane coupling agent and thermocycling

challenge on the shear bond strength between LDS and composite resin. Two-way ANOVA revealed no significant difference in the two factors between the concentrations of silane coupling agents and thermocycling challenge. Therefore, the null hypothesis that there would be no significant difference between the various concentrations of silane coupling agent and thermocycling challenge on the shear bond strength between LDS and composite resin was accepted. Nevertheless, each factor of the silane coupling agent and thermocycling challenge revealed significant differences among the groups. One-way ANOVA and Tukey's HSD were performed to compare all the conditions.

In this study, the effects of different concentrations of the silane coupling agent on the shear bond strength between LDS and composite resin were determined. The results showed that the shear bond strength in the non-thermocycling conditions of the NS group (7.28 MPa) was significantly lower than that of the other groups. The 3%, 6%, 9%, and 12% ESC groups had a significantly higher shear bond strength than the other groups, suggesting that the surface treatment on the LDS surface was a crucial factor in creating a higher shear bond strength between the LDS surface and composite resin. Surface treatment with HF on the LDS surface could remove the glass matrix on the LDS surface, allowing the silane coupling agent and adhesive agent to better penetrate the HF-treated LDS surface, which increased the micromechanical retention and resulted in a statistically high shear bond strength.[3,22] The adhesive agent in this study consists of silane coupling agent which was not affected chemical bonds on LDS surface due to their ineffectiveness, instability, the acidic solution in this adhesive agent promoted homocondensation[23,24], and the others in composition of this one-bottle of adhesive agent i.e. Bis-GMA may inhibit the action of silane by interrupting the forming of siloxane bond to the hydroxyl group of ceramic surfaces.[25]

The characteristics of the silane layer on the LDS surface can affect the shear bond strength between the LDS and composite resin, which consists of chemisorbed and physisorbed layers.[26] The results of this study showed that 6% ESC groups provided the highest shear bond strength due to the chemisorbed monolayer. The chemisorbed layer created a completely bonded monolayer structure of the silanol group on the LDS surface. The lower shear bond strengths of the 1% and 3% ESC groups resulted from a minimal number of silanol groups bonded with the LDS surface, which created an incomplete chemisorbed monolayer. The higher concentrations of MPS in the 9% and 12% ESC groups resulted in decreased shear bond strength. This resulted from the physisorbed layer, which contains weak Van der Waals forces and hydrogen bonds.[27] In addition, after the hydrolysis process, the higher concentrations of silane coupling agent in the 9% and 12% ESC groups tended to cause homocondensation, which created a siloxane bond between the silane molecules, resulting in a minimal number of silanol groups bonded with the LDS surface.[10,28]

The shear bond strength decreased significantly after the thermocycling. The shear bond strengths of the 3%, 6%, and 9% ESC groups were greater than those of the other groups. Previous studies have reported that the moisture of the oral environment induces the hydrolysis of the silane coupling layer, which results in degradation at the adhesive interface.[29] The water molecules entered the silane coupling layers and gradually hydrolyzed the siloxane bonds, resulting in decreased bond strength.[30] In addition, the difference in the thermal expansion coefficients of each material created thermal stress at the interface of the LDS surface, adhesive agent, and composite resin.[29] This study reported that the shear bond strength of hydrolyzed 6% ESC groups gradually decreased over time and was significantly lower than that of the other groups at day 32. These results may be due to the increased level of homocondensation.[10,28]

According to the SEM images of this study, the untreated LDS surface and NS group were similar and showed a smooth surface topography (Figures 3A and 3C). The application of an adhesive agent on a non-etched-LDS surface (NS group) resulted in the lowest shear bond strength. After HF etching, the etched-LDS surface morphology appeared as a typically needle-like crystal. The glassy matrix on the superficial LDS surface was dissolved and exposed to lithium disilicate crystals (Figure 3B). Surface treatment with a silane coupling agent on the etched-LDS surface promoted chemical bonding. However, the chemisorbed monolayer of the silane coupling agent on the etched-LDS surface was not observed in the SEM topography because of the very thin layer (Figure 4B). The fractured LDS surface covered with an adhesive agent and silane coupling agent layer

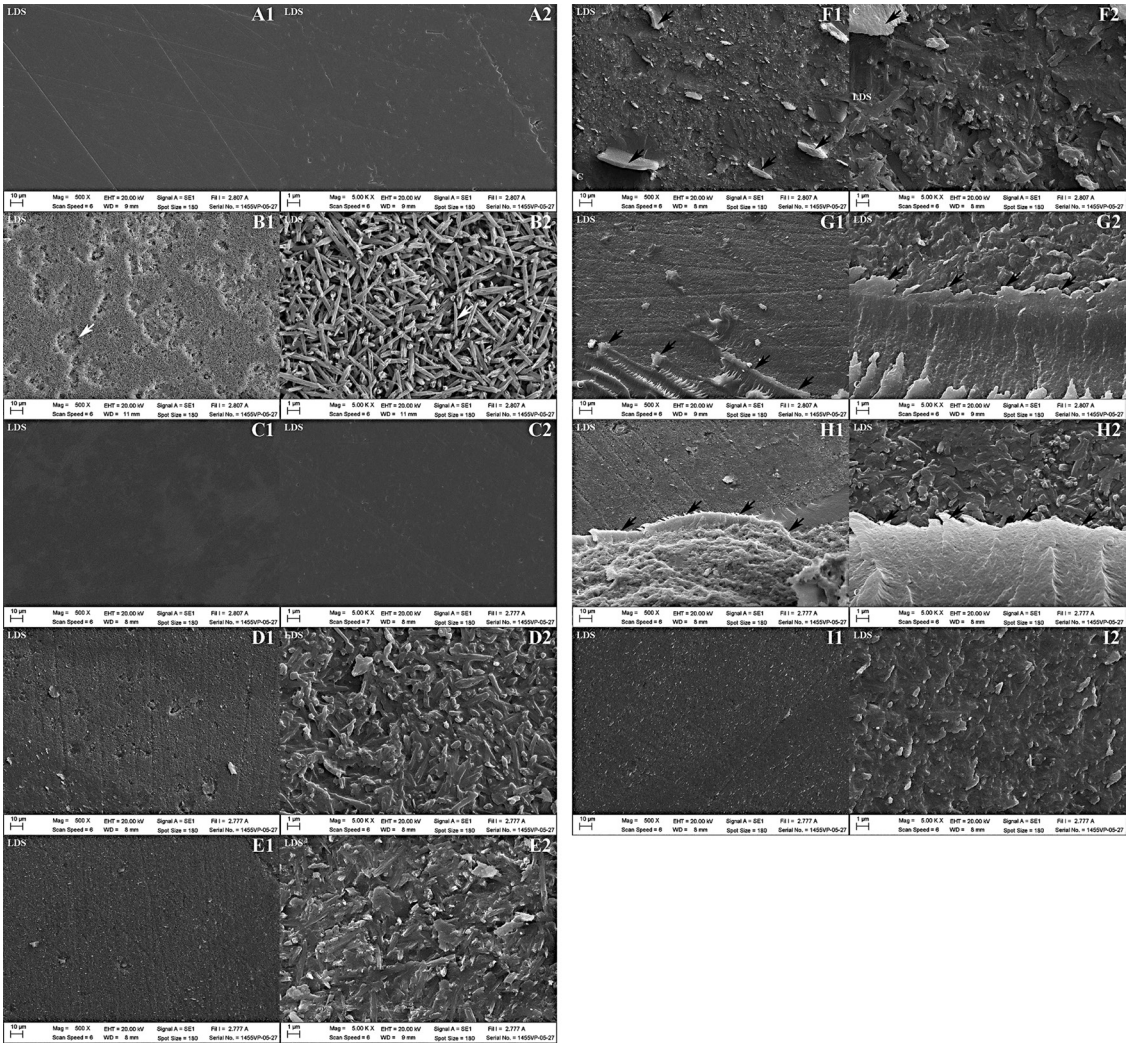


**Figure 3:** Representative SEM images of the fractured LDS surfaces in non-thermocycling condition. Left side of the images show SEMx500 magnification. Right side of the images show SEMx5,000 magnification. (A1, A2) Non-etched LDS surface. (B1) The etched LDS surface. White arrow show the etched pattern. (B2) The etched LDS surface. White arrow show the lithium disilicate glass particles. (C1, C2) Non-silanized LDS surface. (D1, D2) The fractured surface of the CSC group. (E1, E2) The fractured surface of 1% ESC. (F1, F2) The fractured surface of 3% ESC. (G1, G2) The fractured surface of 6% ESC. (H1, H2) The fractured surface of 9% ESC. (I1, I2) The fractured surface of 12% ESC. (F1-H2) Black arrows show the remaining composite resin.

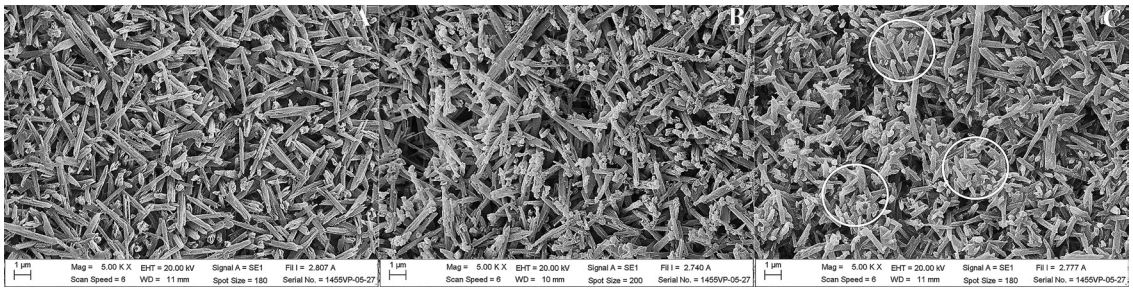


**Figure 4:** Representative 5000 magnifications of SEM images on the LDS surfaces. (A) etched LDS surfaces. (B) etched and silanized with 6% ESC, A and B show exposed needle-like crystal of LDS. (C) etched and silanized with 12% ESC. White circles show the cluster-crystal structure of LDS that was covered with physisorbed layers.

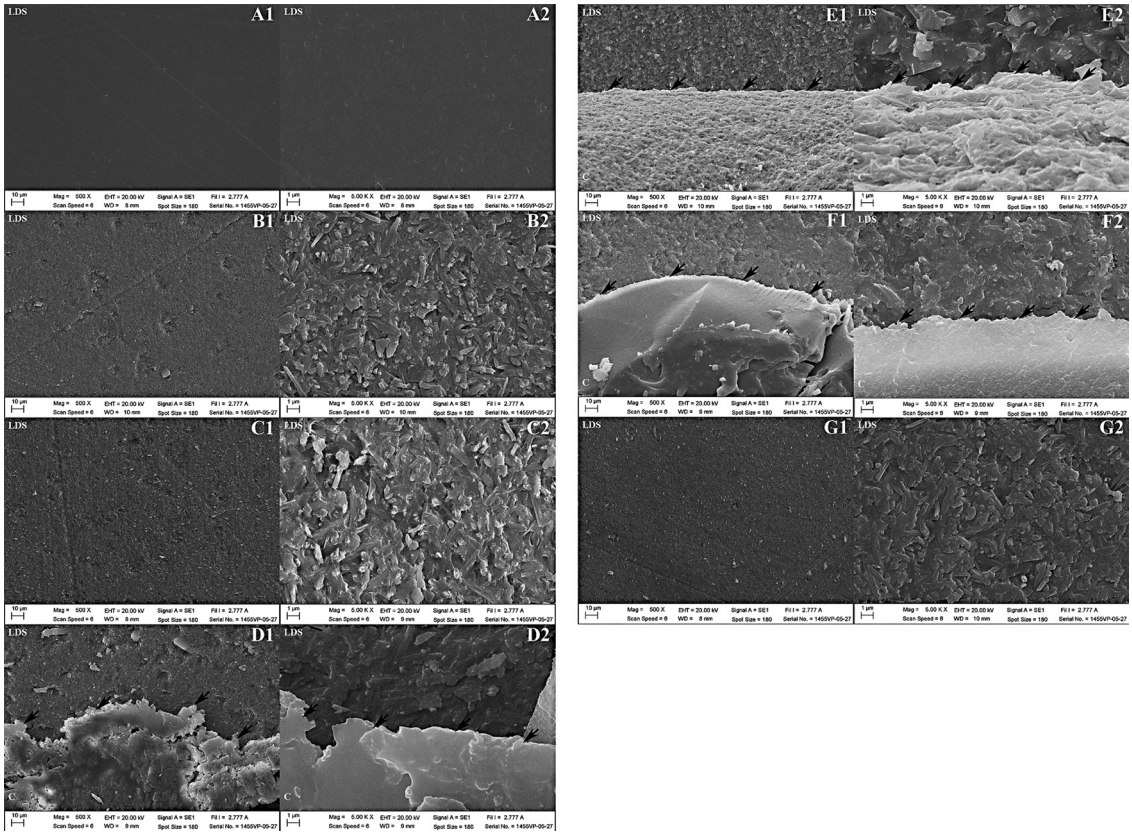


**Figure 5:** Representative SEM images of the fractured LDS surfaces in thermocycling condition. Left side of the images show SEMx500 magnification. Right side of the images show SEMx5,000 magnification. (A1, A2) Non-silanized LDS surface. (B1, B2) The fractured surface of the CSC group. (C1, C2) The fractured surface of 1% ESC. (D1, D2) The fractured surface of 3% ESC. (E1, E2) The fractured surface of 6% ESC. (F1, F2) The fractured surface of 9% ESC. (G1, G2) The fractured surface of 12% ESC. (D1-F2) Black arrows show the remaining composite resin.

was frequently observed in the CSC, 1%, and 12% ESC groups under both non-thermocycling and thermocycling conditions (Figures 3D, 3E, 3I, 5B, 5C, 5G). The absence of the remaining composite resin on the fractured LDS surface after the shear bond strength test indicated an inappropriate chemical bond. These results may be due to the incomplete chemisorbed layer of silanol molecules on the LDS in the 1% ESC group. On the other hand, the excess amount of silanol molecules in the 12% ESC group created physisorbed layers and homocondensation (Figure 4C). After the shear bond strength test, the crack that passed through the physisorbed layer resulted in the absence of the remaining composite resin on the fractured LDS surface.

The fractured surfaces of the 3%, 6%, and 9% ESC groups after the shear bond strength test under non-thermocycling and thermocycling conditions demonstrated a similar trend. The remaining composite resin on the surface of the LDS specimen was observed (Figures 3F-H, 5D-F). This result and the failure modes of the 3%, 6%, and 9% ESC groups were categorized and frequently appeared in the mixed failure mode than in the adhesive failure mode. In addition, all the fracture surfaces of the 6% ESC group in the non-thermocycling and thermocycling conditions demonstrated a mixed failure mode with mean percentages of composite resin remnants of 30.8% and 8.9%, respectively, which showed the highest shear bond strength for each condition.

According to the elemental analysis, the chemical molecular structure of the silane coupling agent contains C, Si, and O elements, whereas the LDS consists of Si and O elements. In other words, Si and O were found in both the LDS surface and the silane coupling agent. Therefore, elemental C was the appropriate element to show that the silane coupling agent reacted with the LDS surface.

After silanization in the unwashed THF condition, the lowest C atom appeared in the 1% ESC group. The C atom gradually increased and reached a peak in the 12%

ESC group. These results may be due to the increasing amount of C atoms, followed by an increase in the silane coupling agent concentration. In contrast, the number of C atoms after THF washing gradually increased from the 1% ESC group and reached a plateau in the 6% ESC group. The plateau atomic % C of ≥6% ESC in the THF washed groups indicated the complete removal of the physisorbed silane coupling agent by THF washing. Therefore, the 6% ESC group was the optimal concentration for creating a chemisorbed layer on the LDS surface.

## Conclusions

Within the limitations of this study, we conclude that 6% ESC provided the highest shear bond strength. This was due to the optimal chemisorbed monolayer formed along with HF surface etching. The shear bond strength decreased significantly after the thermocycling. Moreover, the bond strength of the hydrolyzed silane coupling agent gradually decreased over time, the shear bond strength values at day 0 and 1 were significantly higher than that of day 32.

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## Conflict of interest

The authors declare no conflict of interest.

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