INTRODUCTION

The selection of a ceramic bonding system affects the luting of ceramic restorations. Silica based ceramics exhibit better clinical performance when treated with a silane primer and luted with a resin based luting agent. An appropriate bonding procedure will increase the fracture toughness of the ceramic restorations and maximize the performance. The key to the bonding interface of the silica-based glass ceramic restorations is bonding the luting agent to silicon dioxide. A reliable bonding of the resin-based luting agent to the silica-based ceramic substrate is achieved by micromechanical retention e.g., air-borne particle abrasion, etching of hydrofluoric acid, chemical adhesion via organosilanes.

Over the last few decades, 3-(trimethoxysilyl)propyl methacrylate (3-TMSPMA) has been widely used as a silane primer in clinical dentistry. The main bonding mechanisms of the silane primers have been proposed. It is reported that methoxy groups are hydrolyzed to silanol groups by moisture on the inorganic groups or in the solvent, and the silanol groups condense with surface hydroxyl groups on inorganic particles to form a covalent bond. In addition, it was reported that heat treatment procedures reduce solvents and enhance the cross-linking reaction.

The bonding interfaces are not stable in the oral cavity. Because of the silanized layer of the matrix resin/ceramic interface, hydrolysis occurs and the bonding durability decreased over a long time period. There are several ways to minimize this degradation. One method for solving the degradation is to use a silane coupling agent with high hydrophobicity. Various types of methacrylic silanes are available. Among them, 3-(4-methacryloyloxyphenyl)propyl trimethoxysilane (3-MPPTS) contains a hydrophobic phenyl group. Limited information, however, is available about the influence of intermediate alkyl structures on bonding performance of silane monomers. There are several reports about the influence of bond durability for silane coupling agents with different structures. However, there are few reports on the bond durability to 3-MPPTS. The other methods aim to accelerate the mechanism of chemical interaction between the silane and ceramic surface, such as heat treatment after silanizing.

The purpose of this study was to investigate how different compositions of experimental silane-based primers in a methyl methacrylate solution containing 3-(trimethoxysilyl)propyl methacrylate (3-TMSPMA) or 3-(4-methacryloyloxyphenyl)propyl trimethoxysilane (3-MPPTS) might act as silicon dioxide bonding agents. With or without post-silanization heat treatment, primer-treated quartz discs were bonded using the MMA-TBB resin and their bond strengths were evaluated. The disks were primed with one of the following materials: 1 mol% 3-TMSPMA, 2 mol% 3-TMSPMA, 1 mol% 3-MPPTS, and 2 mol% 3-MPPTS. Shear bond strength was determined both before and after thermocycling. Statistical analyses were performed with non-parametric procedure (Kruskal-Wallis, Mann-Whitney U, and Steel-Dwass tests). Both primers were effective with heat treatment to enhance bonding between quartz and the MMA-TBB, and the bonding durability of the 1 and 2 mol% 3-MPPTS (16.8 and 24.9 MPa) with heat groups was significantly higher than in the 1 and 2 mol% 3-TMSPMA (5.4 and 9.8 MPa) with heat groups.

**Keywords**: Bonding durability, Silane, Silica, Tri-n-butylborane
different compositions of experimental silane-based primers in a methyl methacrylate solution containing 3-TMSPMA or 3-MPPTS might act as silicon dioxide bonding agents. With or without post-silanization heat treatment, primer-treated ceramics were bonded using a tri-\(n\)-butylborane-initiated self-curing luting agent and their bond strengths were evaluated.

The null hypotheses were as follows: (1) each of the different compositions of silane coupling agents would provide the same shear bond strength and durability of self-polymerizing acrylic resin to silicon dioxide; and (2) the use of heat treatment would provide the same shear bond strength and durability to the silicon dioxide.

**MATERIALS AND METHODS**

**Materials**

Materials in this evaluation are listed in Table 1. A fused quartz (SiO\(_2\) 99%, Kokugo, Tokyo, Japan) was used as the adherend material. Two silane compounds were used: 3-TMSPMA (Tokyo Chemical Industry, Tokyo, Japan) and 3-MPPTS. The 3-MPPTS was synthesized according to the procedure reported by Okada et al.\(^\text{11}\). The structural formulae of the silane compounds are shown in Fig. 1. Two experimental silane solutions were prepared in a methyl methacrylate (MMA, Tokyo Chemical Industry) solvent. Each of the silane solutions was diluted 1 and 2 mol% using MMA.

A self-polymerizing resin consisting of a tri-\(n\)-butylborane (TBB) initiator (Super-Bond Catalyst V, Sun Medical, Moriyama, Japan), MMA (Tokyo Chemical Industry), and polymethyl methacrylate (PMMA, Super-Bond Opaque Ivory powder, Sun Medical) was used as a luting agent.

**Specimen preparation and shear bond strength**

A total of 220 disk specimens (10.0 mm in diameter, 2.5 mm in thickness) were prepared for the fused quartz (SiO\(_2\)). The quartz disks cut from rods were supplied by the manufacturers. All disks were wet-ground with a series of silicon carbide paper (600-, 800-, 1200-, and

![Fig. 1 Structural formulae of 3-TMSPMA and 3-MPPTS.](image)

Table 1  Materials assessed

| Materials assessed | Abbr. | Manufacturer | Lot number | Composition (%) |
|--------------------|-------|--------------|------------|-----------------|
| Adherend material  |       |              |            |                 |
| Fused quartz       | Kokugo, Tokyo, Japan | SiO\(_2\) 99.8 |
| Silane compounds   |       |              |            |                 |
| 3-(trimethoxysilyl)propyl methacrylate (3-TMSPMA) | 3-TMSPMA | Tokyo Chemical Industry | DOWOK-TR | 3-TMSPMA 98.0 |
| 3-(4-methacryloyloxyphenyl)propyltrimethoxysilane (3-MPPTS) | 3-MPPTS\(^\text{11}\) | Tokyo Chemical Industry, Tokyo, Japan | | 3-MPPTS 99.0 |
| Solvent            |       |              |            |                 |
| Methyl methacrylate | Tokyo Chemical Industry | 2YRIMJD | MMA 99.8 |
| Luting material    |       |              |            |                 |
| Super-Bond Catalyst V | Sun Medical, Tokyo, Japan | GX41F | TBB, TBB-O, hydrocarbon |
| Super-Bond Opaque Ivory Powder | Sun Medical | KL1 | PMMA, titanium oxide |
| Methyl methacrylate | Tokyo Chemical Industry | 2YRIMJD | MMA 99.8 |

TBB, tri-\(n\)-butylborane; TBB-O, partially oxidized tri-\(n\)-butylborane; MMA, methyl methacrylate; PMMA, polymethyl methacrylate
1500-grit, Wet or dry Tri-M-ite sheet, 3M, St. Paul, MN, USA). Then, all specimens were cleaned with acetone using an ultrasonic bath (SUC-110, Shofu, Kyoto, Japan) for 10 min and kept in a vacuum desiccator for 24 h.

The 220 disk specimens were divided into five sets (n=44): four silane primers and an unprimed control (UP). Then, each group was divided into two groups (n=22): with or without heat treatment using a heat oven (KL-310, Kuraray Noritake Dental, Tokyo, Japan). A piece of double-coated tape with a hole (5 mm in diameter) was placed on the disk surface to define the bonding area. Four silane primers (1 mol% 3-TMSPMA, 2 mol% 3-TMSPMA, 1 mol% 3-MPPTS, and 2 mol% 3-MPPTS) were assessed as the bonding promoter. The disk specimens, without control specimens, were primed with one of the silane coupling agents and air-dried. Half of the primed specimens were heated using an oven at 110°C for 10 min16). A stainless-steel ring (6.0 mm inner diameter, 2.0 mm in height, and 1.0 mm in thickness) was placed around the 5-mm diameter circular hole. The ring was filled with luting agent using a brush dip technique.

All specimens were immersed in distilled water at 37°C for 24 h and randomly divided into two subgroups. Half were subjected to the shear bond strength test (n=11). This state was considered to be 0 thermocycles (Tc=0). The remainder underwent 10,000 thermal cycles with a dwelling time of 60 s between 5 and 55°C water baths (Thermal Shock Tester TTS-1 LM, Thomas Kagaku, Tokyo, Japan) and were then subjected to shear bond strength testing (n=11, Tc10,000). The specimens were then fixed in a steel mold and seated in a bond testing jig. The shear bond strength was determined using a mechanical testing device (Type 5567, Instron, Canton, MA, USA) at a crosshead speed of 0.5 mm/min.

**Statistical analyses**

Statistical analyses were performed with the applications (GraphPad Prism 6.0, GraphPad Software, La Jolla, CA, USA and Kyplot 5.0, KyensLab, Tokyo, Japan). For the shear bond strength data, the median values and interquartile range of the eleven specimens were calculated. The D’Agostino-Pearson omnibus test (GraphPad Prism 6.0) revealed that the shear bond strength data for all groups followed a normal distribution. The Bartlett test (GraphPad Prism 6.0) was used to evaluate the differences among each of the treatments. Steel-Dwass multiple comparisons (Kyplot 5.0) were performed as non-parametric tests to evaluate the differences between groups with and without heat treatment. The statistical significance level was set at α=0.05.

**Failure mode analysis**

After the shear bond testing, the fractured interface of the specimens was observed with an optical microscope (Stemi DV4, Carl Zeiss, Jena, Germany) at ×32 magnification. The failure mode was classified into four categories as shown in Fig. 2.

**Fourier-transform infrared absorption (FT-IR) spectroscopic analysis**

The procedure for spectral measurement is illustrated in Fig. 3. A FT-IR spectrophotometer (FT-IR-400 Plus, Shimadzu, Kyoto, Japan) was used to obtain IR transmission spectra. All spectra were recorded at a resolution of 2 cm⁻¹ throughout the spectral range (4,000–500 cm⁻¹). There were a total of 100 scans. The spectrophotometer was prepared with a KBr (Potassium bromide for IR spectroscopy Uvasol, Merck, Darmstadt, Germany). The absorption spectrum was measured using the KBr tablet method.

Each of the silane compounds (3-TMSPMA and 3-MPPTS) was diluted 2 mol% with MMA (Tokyo Chemical Industry). The specimens were cut from the fused quartz rods. A total of five quartz specimens (10.0 mm in diameter and 0.5 mm in thickness) were prepared. Silane primers (2 mol% 3-TMSPMA and 2 mol% 3-MPPTS) were applied to each of the quartz disk surface and rinsed using MMA by pipette for 1 min. Each group was further divided into the following five groups: Group 1: an unprimed control quartz specimen was rinsed using MMA by pipette for 1 min and air-dried. Group 2: 2 mol% 3-TMSPMA was applied for 1 min, rinsed using MMA by pipette for 1 min, and air-dried. Group 3: 2 mol% 3-TMSPMA was applied for 1 min and dried with heat treatment using a heat oven at 110°C for 10 min, rinsed using MMA by pipette for 1 min, and air-dried. Group 4: 2 mol% 3-MPPTS was applied for 1 min, rinsed using MMA by pipette for 1 min, and air-dried. Group 5: 2 mol% 3-MPPTS was applied for 1 min and dried with heat treatment using a heat oven at 110°C for 10 min, rinsed using MMA by pipette for 1 min, and air-dried.

**Fig. 2** Classification of bond failure modes.

A: Fused quartz-luting agent interface separation,
B: Fused quartz-luting agent separation with crack propagation inside the fused quartz, C: Cohesive failure inside the fused quartz range with fused quartz-luting agent interface separation, D: Fused quartz cohesive failure.
Each of the treated specimens was measured with the KBr method. Treated quartz specimen was milled using mortar until it became powdery. KBr (1 g) and treated quartz powder (15 mg) were mixed and milled more finely. KBr powder and quartz powder were pressed for disk form (10.0 mm in diameter). The results were compared with those of previous reports.[10,25-27]

RESULTS

Shear bond strength

The median shear bond strength values and interquartile rage of each subgroup for the tested silane primers without heat treatment are listed in Table 2. The Tc0 median bond strengths ranged from 1.2 to 25.2 MPa. Tc0-1 mol% 3-TMSPMA, 1 mol% 3-MPPTS, and 2 mol% 3-MPPTS resulted in the highest bond strength (category c). The Tc10,000 median bond strengths ranged from 0.3 to 10.4 MPa. Tc0,000-1 mol% and 2 mol% 3-MPPTS had the highest bond strength (category f).

The results of the shear bond strength with heat treatment are also listed in Table 3. Tc0 median bond strengths ranged from 1.6 to 28.5 MPa. Tc0-1 mol% and 2 mol% 3-MPPTS resulted in the highest bond strength (category i). The Tc10,000 median bond strengths ranged from 0.6 to 24.9 MPa. Tc10,000-1 mol% and 2 mol% 3-MPPTS also had the highest bond strength (category m). Comparison of the Tc0 and Tc10,000 bond strengths revealed that the bond strengths of the all groups differed significantly (Mann-Whitney U test, Tables 2 and 3).

Comparison of the bond strengths with and without heat treatment after thermocycling revealed that the bond strengths of the four groups significantly differed (Table 4).

Failure mode

Evaluation of the failure mode after the shear bond

| Specimens treatment | Rinsing | Mixture | Transmission method |
|---------------------|---------|---------|---------------------|
| 1. Unprimed control quartz was rinsed using MMA by pipette for 1 min. 2. A 2 mol% 3-TMSPMA or 2 mol% 3-MPPTS was applied to the quartz surface. 3. A 2 mol% 3-TMSPMA or 2 mol% 3-MPPTS was applied to the quartz surface with heat treatment using a heat oven at 110°C for 10 min. | All specimens were rinsed using MMA by pipette for 1 min and air-dried. | KBr (1 g) and quartz (15 mg) were mixed and milled more finely. | KBr powder and quartz powder were pressed for disk form. |

Table 2  Shear bond strength between fused quartz (SiO2) and luting agent without heat treatment in MPa

|              | Tc0 | Tc10,000 | M-W | Post-/Pre-ratio (%) |
|--------------|-----|----------|-----|---------------------|
|              | Median | IQR | Category | Median | IQR | Category |                   |
| Unprimed     | 1.2   | 0.7  | a        | 0.3    | 0.2  | d        | S 25               |
| 1 mol% 3-TMSPMA | 22.3  | 13.7 | b        | 0.4    | 0.0  | d        | S 1.8              |
| 2 mol% 3-TMSPMA | 14.8  | 14.5 | b        | 0.5    | 0.2  | e        | S 3.4              |
| 1 mol% 3-MPPTS | 25.2  | 4.7   | c        | 10.4   | 8.8  | f        | S 41.3             |
| 2 mol% 3-MPPTS | 23.6  | 4.4   | c        | 4.0    | 3.9  | f        | S 16.9             |

n=11; IQR, Interquartile range; Identical lower case letters indicate values that are not significantly different (Steel-Dwass multiple comparisons; p>0.05). M-W, Abbreviation “S” indicates that the difference between the pre- and post-thermocycling shear bond strengths is significant (Mann-Whitney U test; p<0.05).
testing indicated that the high bond strength groups tend to show fused quartz cohesive failure (D), while the low bond strength groups tend to exhibit adhesive failure (A) (Table 5). The two silane primers (1 mol% and 2 mol% 3-MPPTS) with heat treatment tended to exhibit (D) after thermocycles. The cohesive failure inside the

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Table 3 Shear bond strength between fused quartz (SiO₂) and luting agent with heat treatment in MPa

|                  | Tc0 Median | IQR | Category | Tc10,000 Median | IQR | Category | M-W | Post-/Pre-ratio (%) |
|------------------|------------|-----|----------|-----------------|-----|----------|------|----------------------|
| Unprimed         | 1.6        | 1.6 | g        | 0.6             | 0.1 | j        | S    | 37.5                 |
| 1 mol% 3-TMSPMA  | 22.9       | 5.4 | h        | 5.4             | 3.1 | k        | S    | 23.6                 |
| 2 mol% 3-TMSPMA  | 21.3       | 6.3 | h        | 9.8             | 4.0 | l        | S    | 46.0                 |
| 1 mol% 3-MPPTS   | 28.5       | 3.0 | i        | 16.8            | 9.7 | m        | S    | 58.9                 |
| 2 mol% 3-MPPTS   | 27.7       | 4.5 | i        | 24.9            | 3.4 | m        | S    | 90.0                 |

n=11; IQR, Interquartile range; Identical lower case letters indicate values that are not significantly different (Steel-Dwass multiple comparisons; p>0.05). M-W, Abbreviation “S” indicates that the difference between the pre- and post-thermocycling shear bond strengths is significant (Mann-Whitney U test; p<0.05).

Table 4 Comparison of bond strengths between heat and without heat treatment after thermocycling

|                  | p-value | M-W |
|------------------|---------|------|
| 1 mol% 3-TMSPMA  | p<0.001 | S    |
| 2 mol% 3-TMSPMA  | p<0.001 | S    |
| 1 mol% 3-MPPTS   | p=0.0064| S    |
| 2 mol% 3-MPPTS   | p<0.001 | S    |

M-W, Abbreviation “S” indicates that the difference between the binary conditions after thermocycling bond strengths is significant. (Mann-Whitney U test; p<0.05).

Table 5 Failure mode with and without heat treatment

|                  | 0 thermocycle | 10,000 thermocycles |
|------------------|---------------|---------------------|
|                  | A  | B  | C  | D  | A  | B  | C  | D  |
| Unprimed         | 10 | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| 1 mol% 3-TMSPMA  | 0  | 0  | 0  | 0  | 11 | 0  | 0  | 0  |
| 2 mol% 3-TMSPMA  | 0  | 0  | 0  | 0  | 11 | 0  | 0  | 0  |
| 1 mol% 3-MPPTS   | 0  | 0  | 0  | 0  | 11 | 0  | 0  | 0  |
| 2 mol% 3-MPPTS   | 0  | 0  | 0  | 0  | 11 | 0  | 0  | 0  |
| with heat treatment |   |   |   |   |     |   |   |   |
| Unprimed         | 10 | 1  | 0  | 0  | 11 | 0  | 0  | 0  |
| 1 mol% 3-TMSPMA  | 0  | 0  | 0  | 0  | 11 | 1  | 4  | 5  |
| 2 mol% 3-TMSPMA  | 0  | 0  | 0  | 0  | 11 | 1  | 0  | 0  |
| 1 mol% 3-MPPTS   | 0  | 0  | 0  | 0  | 11 | 0  | 0  | 0  |
| 2 mol% 3-MPPTS   | 0  | 0  | 0  | 0  | 11 | 0  | 0  | 0  |
luting agent was not detected.

**Infrared absorption spectra**

Figure 4a shows the transmission spectrum of the 3-TMSPMA monomer. The peaks at 2,945 and 2,841 cm\(^{-1}\) resulted from C-H stretching. The strong peak at 1,719 cm\(^{-1}\) is the carbonyl C=O stretching, while the weak peak at 1,638 cm\(^{-1}\) is the C=C stretching. The peaks at 1,320 and 1,296 cm\(^{-1}\) are associated with the ester (-C-O-C-) functionality. The peaks at 1,194 and 1,167 cm\(^{-1}\) are also due to ester vibrations, while the bands at 1,088 and 816 cm\(^{-1}\) result from Si-O asymmetric and symmetric stretching and bending vibrations, respectively.

Figures 4b–d show the transmission spectra of the quartz specimens primed with and without 3-TMSPMA. Group 1 shows the bands at 1,102 cm\(^{-1}\) and 803 cm\(^{-1}\) result from Si-O stretching and bending vibrations (Fig. 4b and Table 6). Group 2 shows a weak peak at 1,634 cm\(^{-1}\) result from the C=O stretching (Fig. 4c and Table 6). Group 3 shows the peaks at 2,947 and 2,841 cm\(^{-1}\) result from C-H stretching. The peak at 1,718 cm\(^{-1}\) is the carbonyl C=O stretching, and the weak peak at 1,636 cm\(^{-1}\) is the C=C stretching (Fig. 4d).

Figure 5a shows the transmission spectrum of the 3-MPPTS monomer. The strong peaks at 1,747 and 1,738 cm\(^{-1}\) correspond to carbonyl C=O stretching, while 1,635 cm\(^{-1}\) is the C=C stretching. The peak at 1,506 cm\(^{-1}\) derived from the aromatic structure \(^{28}\).

Figures 5b–d show the transmission spectra of the quartz specimens primed with and without 3-MPPTS. Figures 4b and 5b (Group 1) are the same. Group 4 shows the peak at 1,734 cm\(^{-1}\) resulting from the carbonyl C=O stretching. The peak at 1,507 cm\(^{-1}\) is derived from the aromatic structure. Group 5 has a peak at 2,930 cm\(^{-1}\) from C-H stretching. The strong peak at 1,736 cm\(^{-1}\) is carbonyl C=O stretching, and the weak peak at 1,636 cm\(^{-1}\) result from the C=O stretching (Fig. 4c and Table 6). Group 3 shows the peaks at 2,947 and 2,841 cm\(^{-1}\) result from C-H stretching. The peak at 1,718 cm\(^{-1}\) is the carbonyl C=O stretching, and the weak peak at 1,636 cm\(^{-1}\) is the C=C stretching (Fig. 4d).

Table 6  Band assignments of the IR spectra of 3-TMPMA and 3-MPPTS

| Assignment                  | Wavenumber (cm\(^{-1}\)) |
|-----------------------------|--------------------------|
| Control                     | Group 1 | Group 2 | Group 3 | Group 4 | Group 5 |
| methyl group\(^{10,26}\)    | -CH₃     | ν (C-H) | —       | —       | —       |
| methyl group\(^{10,26}\)    | -CH₃     | ν (C-H) | —       | 2,947   | —       | 2,930   |
| carbonyl group\(^{27}\)    | C=O      | ν (C=O) | —       | 1,718   | 1,734   | 1,736   |
| methacryloyl group\(^{10,27}\) | C=C      | ν (C=C) | —       | 1,634   | 1,636   | —       | 1,636   |
| aromatic structure\(^{25}\) | C=C      | ν (C=C) | —       | —       | 1,507   | 1,507   |
| silicon oxide               | Si-O     | ν (Si-O) | 1,102   | 1,099   | 1,092   | 1,102   | 1,106   |
| silicon oxide               | Si-O     | δ (Si-O) | 803     | 805     | 814     | 807     | 809     |
cm$^{-1}$ corresponds to C=C stretching (Fig. 5d). The peak at 1,507 cm$^{-1}$ corresponds to aromatic structure.

**DISCUSSION**

The use of the different composition of the silane primers and with or without heat treatment affected the shear bond strength of the resin-based luting agent to quartz. Therefore, the null hypotheses are rejected.

Two different silane compounds (3-TMSPMA and 3-MPPTS) were evaluated in this study. 3-TMSPMA enhanced the chemical bonding to the silica based glass ceramic surface in agreement with previous studies. 3-TMSPMA is usually pre-hydrolyzed and diluted in ethanol-water solution with pH adjusted with acid. There are also two-bottle or three-bottle systems available for immediate hydrolysis in the clinical conditions, which contain 3-TMSPMA, acid, adhesive, and methacrylate. The structural formula of 3-MPPTS is illustrated in Fig. 1. The 3-MPPTS monomer contains a 1,4-phenyl group between methacryloyloxy group and trimethoxysilylpropyl group. The authors used 3-MPPTS as a priming agent for quartz adherend expecting improvement of bonding durability derived from hydrophobicity of phenylpropyl intermediate structure of 3-MPPTS as compared with propyl structure of 3-TMSPMA. In the present study, the experimental silane primers were prepared by mixing only 3-MPPTS compound and MMA monomer. Hence, to activate these silane primers, it is necessary to mix them with an acidic substance or apply heat treatment.

Although the 1 mol% 3-TMSPMA without heat treatment group had a 22.3 MPa pre-thermocycling bond strength, the post-thermocycling bond strength was only 0.4 MPa (Table 2). The 2 mol% 3-TMSPMA without heat treatment group had a similar result. These results suggest when 3-TMSPMA was applied to the quartz surface without heat treatment, no siloxane bond was effectively formed on the quartz surface. The shear bond strength of Tc10,000-1 mol% and 2 mol% 3-MPPTS without heat treatment (category f) was significantly higher than that of 3-TMSPMA (categories d and e) (Table 2). These results suggest when 3-MPPTS was applied to the quartz without heat treatment, a siloxane bond was partially formed on the quartz surface. In Tc0 and Tc10,000, the bond strength of the 3-MPPTS with heat treatment groups (categories i and m) was significantly higher than the unprimed and 3-TMSPMA groups (Table 3). In general, the phenyl silane is used as the purpose of the improvement in the hydrophobicity, containing a benzene ring. The chemical formula of the silane compound 3-MPPTS has higher hydrophobicity than 3-TMSPMA by having replaced a hydrophobic group with a phenyl group (Fig. 1).

Heat treatment of silanated glass is frequently performed in the glass industry to maximize the bond strength. The authors consider that heat treatment accelerated condensation of silanes to form covalent bonds between quartz, and to eliminate methanol and water. From the results of Table 4, it was clear that silane compounds (3-TMSPMA and 3-MPPTS) with heat treatment had significantly higher bond strength than without heat treatment. These results suggested the silanol group in silane coupling agents and the fused quartz surface and a dehydration condensation reaction of fused quartz are promoted by heat treatment. Hydrolyzed alkoxy groups reacted with water to become silanol groups and alcohol molecules are generated as an aside product.

This study used an unprecedented procedure for spectral measurements of an effective silane compound. Silane primers (2 mol% 3-TMSPMA and 2 mol% 3-MPPTS) were applied to each of the quartz disk surfaces and rinsed using MMA with a pipette for 1 min. The spectrophotometer was prepared with KBr. Matinlinna et al. analyzed the structure of 3-TMSPMA adsorbed to a titanium surface using attenuated total reflectance (ATR) spectroscopy. Their results suggested that heat treatment yielded strong absorption bands, peaking for strong siloxane (-Si-O-Ti-) network bonding on the titanium surface. In this study, strong peaks of the silicon oxide group were observed (Table 6). These peaks were derived from siloxane network bonding or fused quartz.

The results of 3-TMSPMA in the heat treatment group (Group 3, Fig. 4d and Table 6) appeared at 2,947 and 2,841 cm$^{-1}$ from carbon-hydrogen stretching vibrations, while the 3-TMSPMA without heat treatment group (Group 2, Fig. 4c and Table 6) did not have peaks at 2,947 and 2,841 cm$^{-1}$. It has been suggested that hydrolysis of the 3-TMSPMA with heat treatment occurred within 10 min.

Nihei et al. and Morikawa reported that phenyl silane was used to improve water proofing and contains a benzene ring. The results of both 3-MPPTS without heat treatment (Group 4, Fig. 5c and Table 6) and 3-MPPTS with heat treatment (Group 5, Fig. 5d and Table 6) appeared at 1,507 cm$^{-1}$ from vibration of the aromatic ring. These results indicate that 3-MPPTS remained on the surface of quartz with and without heat treatment. The C-H out-of-plane bending angle strong peak of the benzene ring was masked by the bending vibration of Si-O and was not observed. However, C=C ring stretching was observed.

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**CONFLICTS OF INTEREST**

The authors declare that they have no conflicts of interest related to this work.

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