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Bond Strength and Water Resistance of a Resin Composite Bonded to Glass Plates Treated with Commercial Ceramic Primers

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Abstract: Background: Silane coupling agents are used as a bonding agent between ceramics and resins in dentistry. The effectiveness of these agents is often enhanced by the addition of acid or by heat treatment. Objective: This study aimed to evaluate, the clinical characteristics, TBS (tensile bond strength) and water resistance of eight commercial ceramic primers (seven silane coupling agents and one alumina zirconia primer). Method: Glass plates were used as the adherent. The TBS of the resin composite and the wettability of the resin monomer to glass surfaces treated with ceramic primers was investigated, with 3-MPS (methacryloxypropyltrimethoxysilane) used as a control. The values obtained from the experiments were analyzed using one-way ANOVA followed by Tukey's multiple comparison tests ($p < 0.05$). Results: No significant differences in TBS were observed between the commercial products and MPS, except for the alumina zirconia primer. However, four products (three of the seven agents and the alumina zirconia primer) exhibited significantly lower TBS values after application of thermal stress when compared with those stored in water ($p < 0.05$). All but one of the eight primers displayed significantly higher contact angles between the treated glass and the resin monomer when compared with MPS ($p < 0.05$). These results suggest that some commercial ceramic primers may contribute to increased strength and durability.

Key words: Silane coupling agent, resin composite, bond strength, bond durability, water resistance, wettability.

1. Introduction

The use of silane coupling agents for the bonding of organic and inorganic substrates is standard practice. In dentistry, silane coupling agents are used as a bonding agent between ceramics and resins, and as a surface treatment for filler particles in resin composites [1-6]. Several commercially available dental ceramic primers contain 3-MPS (methacryloxypropyltrimethoxysilane) as the primary active component. The effectiveness of silane coupling agents is often enhanced by the addition of acid or by heat treatment. However, breakage of siloxane bonds is known to occur after this treatment; the resulting hydrolysis is caused by occlusal stress and thermal or chemical stimulation during food consumption [7-15].

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Previously, we evaluated the water resistance of silane coupling agents by examining the bond strength between resin composite and ceramics or fused silica glass treated with silane coupling agents containing hydrophobic fluorocarbon chains or a phenyl group; significantly higher bond strength and water resistance were observed relative to the samples treated with MPS alone [16-18]. Subsequently, we investigated the bond strength between resin composites and glass surfaces treated with MPS after addition of acid to evaluate the catalytic effect that is known to improve the condensation reaction of silane coupling agents [19]. The use of 5.0 vol% of phosphoric acid resulted in significantly higher bond strength, which was maintained even after thermal stress, indicating the effectiveness of catalyst in improving the activity of the silane coupling agent.

The various forms of dental ceramic primers, include a two-bottle type mixed immediately before application, a one-bottle type with a catalyst, and one that requires acid treatment, all of which contain some type of catalyst.

In the present study, the bond strength of resin composite and the wettability of resin monomer to glass surfaces treated with commercially available ceramic primers were investigated in order to evaluate their clinical characteristics and water resistance and to further understand the efficacy and function of the primers.

2. Materials and Methods

2.1 Materials

Details concerning the eight commercial ceramic primers (seven silane coupling agents and one alumina zirconia primer) used in this study are presented in Table 1. Primers were used according to the manufacturers' instructions as received. MPS (Lot # 206886, Shin-Etsu Chemical, Tokyo, Japan) was prepared as a 50 mmol/L ethanol solution (Wako Pure Chemistry, Osaka, Japan), with 5 vol% phosphoric acid composing 10 vol% of the solution added immediately before application to the glass surface.

2.2 Tensile Bond Strength Tests

Glass plates (15×15×3 mm, Asahi Glass Co., Tokyo, Japan) were used as the adherend. To remove any contamination from the surface, the glass plates were first soaked in 1 mol/L sodium hydroxide solution (Wako Pure Chemistry, Osaka, Japan) for one day, and in 1 mol/L hydrochloric acid solution (Wako Pure Chemistry, Osaka, Japan) the following day. They were then thoroughly rinsed with distilled water, and dried at 50 °C for 2 hours. One surface of the glass plates was treated with each of the eight primers according to the manufacturers' instructions

Table 1 Contents of ceramic primers used in this study.

Material	Manufacture	Code	Composition		Contents
Porcelain Primer	Shofu	IN	one-bottle		silane coupling agent, absolute ethanol, etc.
Monobond S	Ivoclar Vivadent	MO	one-bottle		silane coupling agent(γ-MPTS), ethanol, water, acetic acid
Porcelain Liner M	Sun Medical	PL	two-bottles	liquid A	MMA, 4-META, etc.
				liquid B	MMA, silane coupling agent(γ-MPTS), etc.
RelyX™ Ceramic Primer	3M ESPE	RE	one-bottle		silane coupling agent, ethanol, water
Ceramic Primer	GC	CP	two-bottles	primer A	vinyl silane, ethanol
				primer B	methacrylic acid ester, ethanol
Tokuso Ceramic Primer	Tokuyama Dental	TO	two-bottles	liquid A	silane coupling agent, ethanol
				liquid B	monomer of phosphoric acid, ethanol
Clearfil® Ceramic Primer	Kuraray Noritake Dental	CS	one-bottle		silane coupling agent, MDP, ethanol
AZ Primer	Shofu	AZ	one-bottle		6-methacryloxy hexyl phosphonoacetate, aceton, etc.

using microbrushes (Shofu, Kyoto, Japan). A layer of MPS was applied, and the glass plates were left to dry at room temperature for 5 minutes. An MPS-treated glass plate (no other primer) was used as a positive control, whereas untreated silane (no primer) was used as the negative control. The treated surface of the glass plate was covered with mending tape (Scotch$^{®}$ Mending Tape 810, Sumitomo 3M, Tokyo, Japan) with a round perforation (3 mm diameter) to define the bonded surface. Resin composite (Clearfil^{TM} FII, Paste A and B: Lot # 00061A and 00034A, Kuraray-Noritake, Tokyo, Japan) was mixed according to the manufacturer's instructions and placed on the bonding surface of a mesh type stainless steel rod 5 mm in diameter (Tomy International, Tokyo, Japan). The glass surface and the rod were manually held together for a few minutes to achieve bonding after which the specimens were left in the air at room temperature for 30 minutes. Ten samples of each primer and the positive and negative controls were prepared, and divided into two different immersion groups. Half of the samples were stored in distilled water at 37 °C for 7 days (DW group), and the other group was subjected to thermal cycling (4-60 °C, 40-second dwell time, ×10,000) after storage in distilled water at 37 °C for 1 day (TC group). The tensile bond strength of each sample was measured using an Autograph (AGS-500, Shimadzu, Kyoto, Japan) at a crosshead speed of 1 mm/min.

2.3 Contact Angles of Resin Monomer on Treated Surface

Resin monomer prepared by mixing bisphenol A-glycidyl methacrylate (bis-GMA, Lot # 11-29-17, Monomer-Polymer & Dajaac Labs, Trevose, PA, USA) and triethyleneglycol-dimethacrylate (TEGDMA, Lot # GD01, Tokyo Chemical Industry, Tokyo, Japan; weight ratio of 1:1) was dropped onto the treated glass plates. The contact angles for each sample were obtained using an automatic contact angle-measuring device (DCA-VZ, Kyowa Interface Science, Saitama, Japan).

2.4 Statistical Analysis

The values obtained from the experiments were analyzed using one-way ANOVA followed by Tukey's multiple comparison test ($p < 0.05$).

3. Results

3.1 Tensile Bond Strength

The tensile bond strength between resin composite and treated glass plate for each sample is shown in Fig. 1. Fig. 2 illustrates the type of bond failure at the fracture surface after tensile testing.

The bond strength of the MPS alone was 13 MPa after water immersion with no significant decrease after application of thermal stress (9 MPa; $p > 0.05$). The MPS control specimens demonstrated cohesive failure of the resin composite or fracture of the glass after tensile testing; however, the occurrence of complex failures was more common under thermal stress. As expected, the bond strength of the negative control was 4 MPa, which was significantly lower than that of MPS ($p < 0.05$). It was not possible to measure the bond strength of the negative control after thermal stress owing to the detachment of all the stainless steel rods from the glass surface (adhesive failure) during the experiment.

The bond strengths of all of the ceramic primers (except for alumina zirconia, AZ) were above 10 MPa, after water storage, showing no significant difference from that of MPS alone ($p > 0.05$). No significant decrease in bond strength after thermal stress was observed when compared to the water storage group ($p > 0.05$) for IN, MO, PL and RE. Nevertheless, the values for CP, TO and CS were lower than 6 MPa after thermal stress, which is a significant decrease when compared with the water storage samples ($p < 0.05$). The bond strength of the AZ primer after water storage was significantly lower than MPS ($p < 0.05$) at 4 MPa; the value after thermal stress could not be

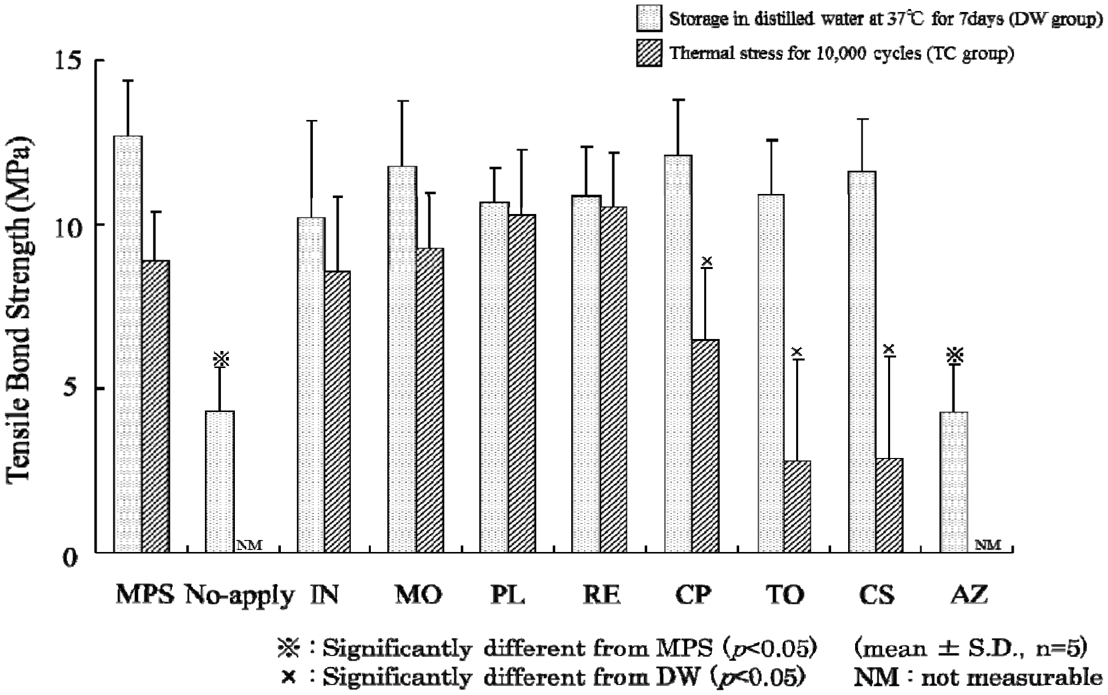


Fig. 1 **Tensile bond strength of resin to glass plates treated with each ceramic primers. A positive control group is MPS (3-methacryloxypropyltrimethoxysilane), a negative control group is no-apply (no silane treatment).**

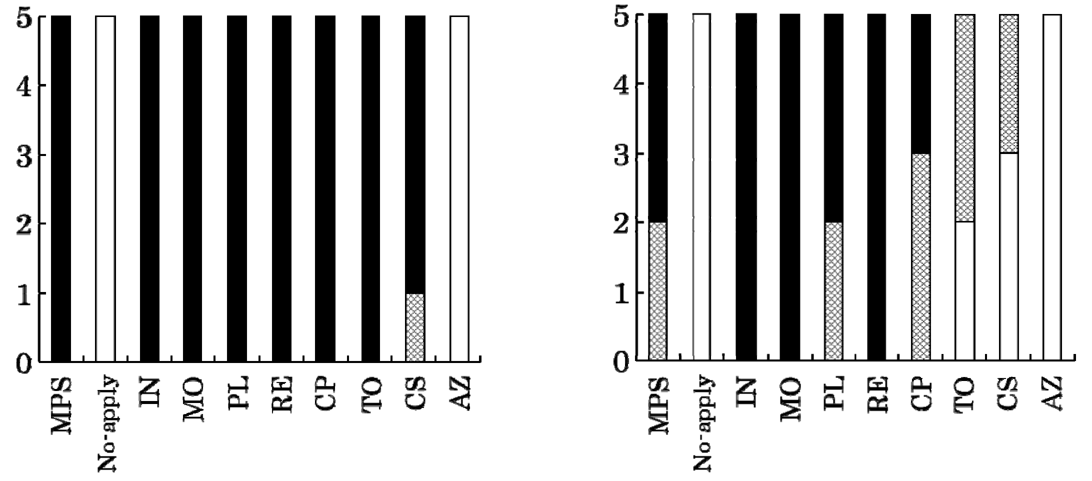


Fig. 2 **The types of fractured surface after tensile bond test. No-apply and AZ groups were adhesive failure in all specimens, and the other groups were increased more common complex failure after thermal stressed.**

measured due to adhesive failure.

All samples primarily demonstrated either cohesive failure in the resin composite or glass fracture on the fractured surface of the commercial silane coupling agent after tensile testing. On the other hand, after thermal stress, there was an increased incidence of complex or adhesive failures between the resin composite and the glass surface. Following thermal stress application, the IN, MO and RE specimens exhibited cohesive failures of the resin composite or glass fractures, whereas the TO and CS specimens presented with increased adhesive failures between the resin composite and glass surface. All AZ specimens underwent adhesive failure between the resin composite and glass surface in both DW and TC groups.

3.2 Wettability of the Resin Monomer on Treated Glass Plates

The contact angles of the resin monomer applied to the treated and untreated glass plates are displayed in Table 2. As expected, the contact angle of the negative control (34.8º) was significantly higher than that of MPS (20.8º; $p < 0.05$). The contact angles of PL and AZ were approximately 21º, not significantly different from MPS ($p > 0.05$). However, in the remaining six commercial ceramic primers, the contact angles ranged between 23º and 40º, and were significantly higher than that of MPS ($p < 0.05$).

4. Discussion

Silane coupling agents are silicon-based chemicals that contain organic substances. In general, they are used as coupling agents to facilitate the adhesion of organic and inorganic materials. In dentistry, silane coupling agents are indispensable in various clinical situations; for example, during the use of resin composites as restorative materials, silane coupling agents are utilized as surface treatments for the filler particles [1]. In addition, they are used for the bonding of glass ceramic restorations, the repair of crowns with resin facings or as a pretreatment material in resin crowns. However, the surface layer treated with silane coupling agents is subjected to thermal changes, water contamination, and intermittent mechanical stress due to eating, brushing, and simple occlusion. The harsh environment of the oral cavity is thought to cause deterioration in the physical properties of the treated layers over time [7-15].

In the present study, the clinical characteristics including the hydrolytic stability of commercially available ceramic primers were evaluated in terms of bond strength and wettability. As shown in previous studies [17, 19], MPS undergoes a decrease in tensile bond strength after thermal stress relative to water storage, but the difference observed was not significant ($p > 0.05$). On the other hand, the proportion of complex failures during tensile bond test increased significantly after thermal stress suggesting that the siloxane bond in the silane-treated layer was broken due to thermal stress, resulting in a decrease in bond strength and an increase in complex failures at the fracture surface. Since chemical bonding was not accomplished between the resin composite and the glass surface in the negative control, the bond strength after DW storage was significantly lower than that seen in MPS ($p < 0.05$). The stainless steel rods had detached from the glass surface during TC storage. Moreover, all negative control specimens exhibited adhesive failure after DW storage and TC storage.

For the AZ primer, similar trends to the negative control were found with respect to tensile bond strength and fracture type after bond strength testing. This may be attributed to the fact that the AZ primer does not contain a silane coupling agent, and therefore, similar to the negative control, no chemical bonding was established. On the other hand, the seven commercial ceramic primers exhibited tensile strengths greater than 10 MPa after DW storage, though not significantly different from MPS. All except for CS presented with cohesive failure in the resin composite or glass fracture after tensile bond strength testing. The manufacturers did not disclose the concentrations of the silane coupling agents (although AZ contains

Table 2 Contact angles of resin monomer on treated glass plates.

	MPS	No-apply	IN	MO	PL	RE	CP	TO	CS	AZ
Contact angle (°)	20.8	34.8*	25.8*	30.0*	20.8	27.8*	39.3*	23.2*	25.3*	21.4
S.D.	0.5	1.3	0.3	0.9	0.5	0.6	0.7	0.8	0.4	0.8

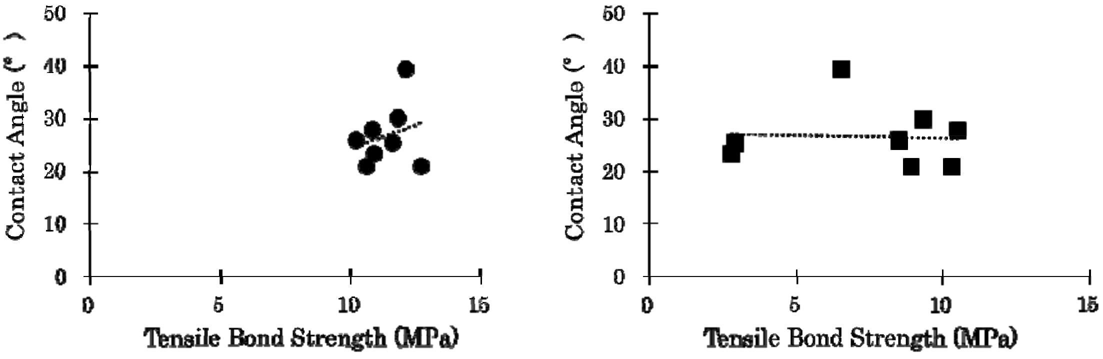
* Significantly different from MPS ($p < 0.05$).

0%; Table 1). Clearly, they have developed their products taking stability and adhesiveness into account, and the bond strength of their products is comparable to MPS alone as a positive control. However, the tensile bond strengths of IN, MO, PL and RE, after TC storage, were not significantly decreased relative to the values obtained after DW storage, demonstrating a higher level of bond strength than MPS alone. Although some PL specimens displayed increased complex failure after tensile testing, the others (IN, MO and RE) exhibited either cohesive failure in the resin composite or glass fracture. The tensile bond strengths of CP, TO and CS after TC storage, were significantly lower than the values obtained after water storage ($p < 0.05$) with an increase in the proportion of complex or adhesive failures. In addition, it was difficult to determine any trends based on primer composition. It has been reported that silane coupling agents, especially the one-bottle types, tend to lose their clinical efficacy over time due to a condensation reaction, a recognized behavior in silanes [20]. However, the ceramic primers used were all freshly manufactured, and no differences in water resistance in terms of bond strength were noted between the one-bottle and two-bottle types. We believe that the results of the afore-mentioned study might have been different if older samples of commercial ceramic primers had been used.

The negative control had a significantly higher contact angle between the glass surface and the resin monomer when compared with MPS ($p < 0.05$). There was no correlation between wettability and bond strength in the commercial ceramic primers (Fig. 3). Yamaguchi [21] reported that bond strength was improved by low contact angles with high wettability, but the results of the present study do not support these findings. It can be assumed that additives and variations in concentration of the commercial ceramic primers used may have affected the results.

Meng et al. [22] reported no correlation between the silane concentration and the siloxane quantity of commercial silanes, as analyzed by FTIR. They reported that silane activation and condensation are affected not only by silane concentration, but also by the solvent. Moreover, they reported a negative correlation between the contact angle of the bonding agent to a silanized ceramic surface and bond durability, and no correlation between siloxane quantity and bond durability. Thus, it was suggested that commercial ceramic primers possess the required amounts of bond durability and wettability for a resin monomer due to the variety of silane components.

We have previously reported that the water resistance of a silane coupling layer is affected by cross-linking in the silane layer, owing to differences



Storage in distilled water at 37℃ for 7 days

Thermal stress for 10,000 cycles

Fig. 3 Correlation diagrams of tensile bond strength and contact angle. There was no correlation between wettability and bond strength in the ceramic primers.

in the hydrolyzable groups of various silanes [17]. The results of this study suggest differences in the cross-linking of commercial ceramic primers. In previous studies, the hydrolysis reactions of single-bottle silane have been shown to be superior to that of the two-bottle silane coupling agents; on the other hand, two-bottle silanes was higher shown to be higher durability [23]. However, the findings of the present study are not in accordance with these results. No differences in bond strength, durability or wettability were observed between the single-bottle and two-bottle primers in this study.

The results presented herein demonstrate that there is no significant difference in bond strength among commercial ceramic primers, but there is a significant difference in the water resistance of these bonds, with variations depending upon the specific primer used. The various proprietary catalysts that promote the reaction of the silane coupling agents are components that may affect the bond strength and water resistance. It is suggested that the use of catalysts in ceramic primers should be evaluated for the optimum performance of these products.

5. Conclusion

The clinical characteristics and durability of eight ceramic primers (seven commercial silane coupling agents and one alumina zirconia primer) were evaluated by measuring the wettability of a resin monomer and the bond strength between a resin composite and a glass surface.

(1) There was no significant decrease in tensile bond strength after thermal stress for MPS (control) relative to storage in water.

(2) No significant decrease in tensile bond strength after thermal stress was found in IN, MO, PL and RE commercial ceramic primers relative to water storage.

(3) There was no significant correlation between wettability and bond strength in the commercial ceramic primers.

These findings suggest that some commercially available ceramic primers might contribute to bond durability more than others.

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Conflict of Interest Statement

The authors have no conflicts to report with respect to this work.

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