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Short- and Long-Term Bond Strength Between Resin Cement and Glass-Ceramic Using a Silane-Containing Universal Adhesive

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Clinical Relevance

Use of various "silane solutions" provides different bond strength values and patterns of failure according to subjection to short- or long-term water storage. Use of an adhesive layer following a separate silane application may improve long-term clinical ceramic/resin cement bonding performance.

SUMMARY

This study aimed to evaluate the effect of various silane-containing solutions on bonding between resin cement and glass ceramic after 24 hours and after six months of water storage. Glass-ceramic plaques (IPS e.max CAD) were sandblasted with aluminum oxide, etched with 10% hydrofluoric acid (HF), and divided into five "silane treatment" groups: RelyX Ceramic Primer (RCP), RelyX Ceramic Primer and Single Bond Plus (RCP+SB), Scotchbond Universal (SBU), Clearfil Ceramic Primer (CP), and no solution (HF-only control). Each group was divided into two "storage time" subgroups: 24 hours or six months in 37°C water. Eighteen resin cement cylinders (RelyX Ultimate) were bonded to each treatment group substrate (n=18) and then subjected to microshear testing. Failure mode was analyzed using scanning electron microscopy. Debond data were analyzed using a two-way analysis of variance and the Tukey *post hoc* test (α=0.05) as well as Weibull distributions. The factors "silane treatment," "storage time," (p<0.0001), and their interaction were statistically significant (p<0.0010). Group means (MPa±SD), RCP (24 hours: 27.2±3.1; six months: 18.0±4.9), and HF-only control (24 hours: 21.1±3.4; six months: 15.7±5.8) showed a reduced bond strength after six months of water storage, while RCP + SB (24 hours: 23.4±4.4; six months: 22.2±5.4), SBU (24 hours: 18.8±3.0; six months: 17.2±3.6), and CP (24 hours: 21.7±4.3; six months: 17.4±4.8) remained

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constant. Weibull analysis revealed that more reliable bond strengths were obtained after six months for SBU and RCP + SB. Evaluation by scanning electron microscopy revealed that all groups demonstrated hydrolytic degradation at six months of storage, but RCP + SB and SBU indicated less. Use of a separate application of silane and adhesive system improved short and long-term ceramic/resin cement bond strength.

INTRODUCTION

In recent years, all-ceramic restorations have been highly utilized in dentistry because of their biocompatibility, high mechanical properties, and optimal esthetics.[1] However, in order to bond inorganic restorative materials to organic tooth tissues, surface preparation and application of coupling agents[2] to both dental tissues[3] and ceramic material are essential.[4] Also, the presence of an intermediate material, such as resin cement, can improve the overall mechanical behavior of the restoration.[5,6] All of these factors need to be considered to ensure adequate, long-lasting bonding with optimal clinical performance.[7]

Two main strategies are employed to enhance resin cement/glass-ceramic bonding: mechanical and chemical. Silanes provide chemical adhesion to silica-containing ceramic substrates[5] and are often coupled with the use of acid etchants on ceramic surfaces (hydrofluoric acid [HF]) in order to dissolve part of the glassy phase, facilitating mechanical interlocking of the resin cement.[4,5,8,9] This combination of both mechanical and chemical strategies is currently the most accepted procedure for enhancing resin cement/glass-ceramic bonding.[2,4,5]

Silane coupling agents have been applied as adhesion promoters in dentistry since 1977.[10] These silane primer molecules contain two different, reactive functional groups: one end reacting with methacrylates and the other reactive toward silica in glassy structures. This latter group can exist as a nonfunctional silane (containing alkoxy [-OR] groups) that, after hydrolysis, reacts with inorganic substrates[2] in order to achieve not only a linear but also a three dimensional, cross-linked network between ceramic and resin.[11-13] The alkoxy groups of silane-coupling agents must be activated by a hydrolysis process (SiOR→SiOH) to be able to bond to silica in glass ceramic through OH groups, following a condensation step in which water is released.[2]

Other methods can also be used to improve ceramic-resin bonding, such as airborne-particle abrasion with 50-μm aluminum oxide[5,14] and employment of primers containing silane mixed with phosphate acid monomers, such as 10-methacryloyloxydecyl dihydrogen phosphate (MDP). These phosphate acid monomers are used because of their ability to chelate bond with metallic cations present in some ceramics (mainly the polycrystalline ceramics) as well as in hydroxyapatite while having the ability to covalently bond with methacrylate groups of resin cements.[14,15] Thus, when silane and a phosphate acid monomer are combined in a ceramic priming agent, a "universal ceramic primer" is created because it has the potential to chemically bond to a high number of restorative and tooth substrates.

Thus, these phosphate acid monomers are also found in some enamel-dentin adhesives (self-etch or multimode) to act as coupling agents between composite resin and calcium present in hydroxyapatite of dental tissues.[16] Silane is incorporated in those adhesives, providing a class of materials called "universal bonding solutions," and are to be used with enamel, dentin, ceramic, and metal substrates. Because silane and MDP are incorporated into those adhesive compositions, these products may also be indicated to enhance bonding between resin cements and glass and nonglass ceramics. Therefore, these universal systems have a great potential for providing adhesion to a wide variety of substrates and for simplification of many dental procedures through use of only one product for many clinical purposes.[17]

Manufacturers recommend this broad range of "silane primers" to be employed indistinctly (whether silane is mixed with other components or not) when performing glass-ceramic pretreatment. To date, there is no evidence comparing the effect of these different kinds of silane primers (particularly the silane-containing, multimode adhesives with conventional silane-only primers) on glass-ceramic/resin cement bonding after short- and long-term storage.

Thus, the purpose of this *in vitro* study was to evaluate the effect of a silane-containing, universal adhesive on the microshear bond strength between resin cement and glass ceramic after 24 hours and after six months of water storage. The null hypotheses tested were 1) that there are no significant differences in ceramic/resin cement bond strengths provided by the different silane treatments employed and 2) that there are no significant differences in ceramic-resin cement bond strengths after 24 hours and after six months of water aging.

METHODS AND MATERIALS

Specimen Preparation and Group Division

One hundred and eighty sintered plaques of lithium disilicate glass ceramic (IPS e-max lithium disilicate CAD/CAM, A2 color, Ivoclar, Vivadent, Schaan, Liechtenstein), measuring 3 ± 0.1 mm in length, 3 ± 0.1 mm in width, and 2 ± 0.1 mm in thickness, were prepared. Specimens were sandblasted with aluminum oxide (50 μm; Bio-Art, São Carlos, Brazil) at 2 bar pressure for five seconds on only one surface at a working distance of 5 mm in order to standardize ceramic surface roughness after the milling process. Specimens were ultrasonically cleaned for five minutes in distilled water and air-dried. Surfaces were then etched with HF (10% hydrofluoric acid gel, Porcelain Conditioner Dentsply, Petropolis, Brazil) for 20 seconds.[18] A previously perforated, double-faced adhesive tape (having circular perforations measuring the same as the resin cement cylinders to be built) was placed on each ceramic surface in order to delineate the ceramic/resin cement bonding area (one cylinder per ceramic plaque).

A variety of manufacturer-recommended silane treatment protocols for the ceramic surfaces were formed among five groups: 1) RelyX Ceramic Primer (3M ESPE, St Paul, MN, USA) consisted of a single silane primer (RCP) and was applied actively onto the ceramic surface for 60 seconds, followed by thorough drying using oil-free air until complete solvent evaporation (20 seconds); 2) RelyX Ceramic Primer was also applied actively for 60 seconds and thoroughly dried, and then an adhesive system (Adper Single Bond Plus, 3M ESPE) was applied in one coat for 15 seconds, air-dried for five seconds, and left unpolymerized in order to be light cured together with the resin cement (RCP+SB); 3) Scotchbond Universal (SBU), a "silane-containing," universal adhesive system (3M ESPE), was actively applied for 20 seconds, air-dried for five seconds, and also left unpolymerized; 4) Clearfil Ceramic Primer (CP), containing both silane and MDP (Kuraray Noritake Inc, Okayama, Japan), was applied to the ceramic surface in one coat and air-dried until solvent evaporation (20 seconds); and 5) a control, HF-only treatment group (HF-control), having no silane treatment, using only the previously HF-etched ceramic surfaces. Materials used are described in Table 1.

Thirty-six resin cement cylinders (RelyX Ultimate, 3M ESPE) (1±0.1 mm in diameter and 1±0.1 mm in height) were built up on treated ceramic surfaces for each group (one specimen was bonded to only a single ceramic plaque) with the aid of a silicon mold containing a single circled compartment per plaque. Resin cement was injected onto the mold using the manufacturers' auto-mixing tip, without separating the tip from the dispensed mass, until filling the compartment completely. A half-millimeter-thick glass slide was then placed over the top of the mold, and each cylinder was exposed for 40 seconds (Optilight Max, Gnatus, Brazil; light output: 600 mW/cm^2). The ceramic-plaque/resin-cement assemblies were removed from the molds after five minutes, water rinsed, and dried. All groups were randomly divided into two subgroups (n=18) for testing the effect of water storage duration at 37°C: 1) 24 hours and 2) six months.

Microshear Bond Strength Test and Statistical Analysis

After each storage time, specimens were dried and attached to a holding device using cyanoacrylate cement (420 Super Bonder Instant Adhesive, Loctite, Henkel Corp, Westlake, OH, USA) and placed on the platen of a universal testing machine (Instron 4411, Instron Corp, Canton, MA, USA) to perform microshear bond testing (μSBS), following methodology developed by Shimada and others.[19] An uplifting shear load was applied to the extreme base of each resin cement cylinder at a crosshead speed of 0.5 mm/min through the aid of a thin wire (0.20-mm diameter) placed strictly parallel to and in contact with the adhesion area on the substrate. Using the cross-sectional area of each specimen, the resulting bond strength was calculated and expressed in MPa, after which a group mean was computed (n=18). All data were statistically analyzed (Minitab version 17.2.1, Minitab Inc, State College, PA, USA). A two-way analysis of variance (silane treatment vs storage time) was performed followed by the Tukey pairwise *post hoc* test at a preset alpha of 0.05 to evaluate bond strength values. Pretesting bond failures were not considered in the statistical analysis. In addition, Weibull distribution plots were also generated. Failure mode prevalence was statistically analyzed using the chi-square test (α=0.05) to assess the effect of silane treatment on failure mode within each storage time.

Failure Pattern Analysis

Visual analysis of the fractured surfaces was performed using scanning electron microscopy. Specimens were mounted on aluminum stubs,

Table 1: *Materials Used and Their Compositions*

Material	Type of Material	Manufacturer/Lot Number	Composition[a]	Application Steps
IPS e.max CAD	Lithium disilicate glass ceramic, A2	Ivoclar, Vivadent, Schaan, Liechtenstein/N76665	SiO_2 , Li_2O, K_2O, P_2O_5, ZrO_2, ZnO, Al_2O_3, MgO, coloring oxides	
RelyX Ceramic Primer (RCP)	Ceramic primer (silane)	3M ESPE St Paul, MN, USA/N406850	MPS, ethanol, water	Apply actively for 60 s, then thoroughly air-dry
Adper Single Bond Plus (SB)	Total-etch adhesive system	3M ESPE/N334650BR	Bis-GMA, HEMA, dimethacrylates, ethanol,water, photoinitiators, a methacrylate functional copolymer of polyacrylic and polyitaconic acids and silica nanofiller	Apply actively for 15 s in one layer and air-dry for 5 s and do not polymerize separately
Scotchbond Universal (SBU)	Multimode adhesive system	3M ESPE/504115	MDP, dimethacrylate resins, HEMA, Vitrebond TM Copolymer, filler, ethanol, water, initiators, silane	Apply actively for 20 s and air-dry for 5 s and do not polymerize separately
Clearfil Ceramic Primer (CP)	Ceramic primer	Kuraray Noritake Dental Inc, Okayama, Japan/ 00023D	MPS, MDP, ethanol	Apply on the entire surface, then thoroughly air-dry
RelyX Ultimate	Resin cement, A2	3M ESPE/505370	Base paste: methacrylate monomers, radiopaque silanated fillers, initiator, stabilizer, rheological additives Catalyst paste: methacrylate monomers, radiopaque alkaline (basic) fillers, initiator, stabilizer, pigments, rheological additives, fluorescence dye, dark cure activator for Scotchbond Universal	Apply the resin cement with an automixing tip (provided by manufacturer) without separating it from the dispensed mass until filling the compartment

Abbreviations: Bis-GMA, bisphenol A-diglycidyl ether dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; MDP, 10-methacryloyloxydecyl dihydrogen phosphate; MPS, methacryloxypropyltrimethoxysilane (pre-hydrolyzed silane).

[a] *Product composition according to materials safety data sheets provided by the manufacturers.*

sputter coated with gold/palladium (SCD 050, Balzers, Schaan, Liechtenstein), and then examined using scanning electron microscopy (SEM) (JSM 5600 LV, JEOL, Tokyo, Japan) operating at 15 kV and a working distance of 15 mm. Images of representative areas of the fractured surfaces were obtained at different magnifications for fracture pattern morphology evaluation. Fracture classification was assigned using the following criteria: AD-CC, adhesive failure between ceramic and resin cement; AD-AC, adhesive fracture between the adhesive system layer (when employed) and the resin cement; C-AS, cohesive failure in adhesive system (when employed); C-CE, cohesive failure within the ceramic; C-RC, cohesive failure in resin cement; and MIX, a mixture of different kinds of fractures within the same specimen.

RESULTS

The statistical report indicated data were normally distributed (Anderson-Darling test, $p=0.251$), and homoscedasticity was proven (Bartlett test, $p=0.080$), both at a preset alpha of 0.05, indicating appropriate use of parametric methods for data analysis. The two-way analysis of variance revealed that the factors "Storage Time" and "Silane Treatment" both significantly influenced μSBS values ($p<0.0001$). Likewise, the interaction between the two factors was also significant ($p=0.0010$). Descriptive statistics for the μSBS results and statistical grouping of data sets for each experimental group are provided in Table 2. Regarding groups stored for 24 hours, the conventional silane (RCP) group presented higher bond strength values than all other experimental groups, except for the group where a

Table 2: *Microshear Bond Strength Values (MPa, mean± SD) Among the Test Groups Stored for Either 24 Hours or Six Months in 37°C Water*

Ceramic Silane Treatment[a]	Storage Time (37°C Water)	N[b]	Number of Pretest failures	Micsoshear Bond Strength (MPa)[c]	Decrease in Bond Strength With Storage Time (MPa [%])	Statistical Grouping Within Storage Time[d]
RCP	24 h	18	0	27.2 (±3.1)	9.2 (34%)	A
	6 mo	18	1	18.0 (±4.9)		ab
RCP + SB	24 h	18	0	23.4 (±4.4)*	1.2 (5%)	AB
	6 mo	18	0	22.2 (±5.4)*		a
SBU	24 h	18	0	18.8 (±3.0)*	1.6 (9%)	B
	6 mo	18	2	17.2 (±3.6)*		b
CP	24 h	18	0	21.7 (±4.3)*	4.3 (20%)	B
	6 mo	18	0	17.4 (±4.8)*		b
HF-control	24 h	18	0	21.1 (±3.4)	5.4 (26%)	B
	6 mo	18	1	15.7 (±5.8)		b

[a] *RCP, RelyX Ceramic Primer; RCP + SB, RelyX Ceramic Primer and Adper Single Bond 2; SBU, Single Bond Universal; CP, Clearfil Ceramic Primer; HF/control, no silane, 10% hydrofluoric acid only.*

[b] *Sample size.*

[c] *Debond strength values with an asterisk between 24 hours and six months for each treatment are not significantly different.*

[d] *For statistical grouping, groups identified by similar uppercase letters (24-hour values) or lowercase letters (six-months values) are not significantly different* ($p \leq 0.05$).

conventional silane followed by an adhesive system layer was applied (RCP+SB), which also showed no statistical difference with the other groups (Table 2). Moreover, after six months of water storage, the RCP + SB and RCP groups obtained the highest results (respectively), but RCP was not statistically different from the other groups (CP, SBU, and HF-control) (Table 2). Only the RCP and the HF-control groups demonstrated a significant decrease in bond strength values between 24 hours and six months of water storage, while groups RCP + SB and SBU presented more stable and uniform data distributions for this comparison (Table 2).

Weibull distributions are graphically presented in Figure 1, and associated parameters are summarized in Table 3. The analysis showed, in general, that after 24 hours of aging, all groups were more reliable (higher Weibull modulus) and presented higher characteristic bond strengths (higher scale value) than after six months of storage (Table 3). Accordingly, the Weibull distributions after 24 hours of storage appear more vertical (higher slope, m), and bond strengths appeared more toward the higher end of strength values (on the right side of Figure 1) than were plots of similar bonding conditions but stored for only six months. The highest modulus and characteristic strength values were recorded for RCP/24 hours (10.8 and 28.5, respectively), and the lowest were seen using the HF-control/six months (3.1 and 17.6, respectively) (Table 3). Groups CP and SBU presented the least variation among Weibull moduli, and groups RCP + SB and SBU demonstrated the least variation in characteristic strength between the two aging conditions (Table 3; Figure 1). Conversely, groups RCP and HF-control demonstrated the most change in Weibull parameters between the two storage durations (Table 3; Figure 1).

The chi-square test revealed that failure mode is affected by silane treatment for both storage conditions ($p<0.0001$). The failure analysis results (Figure 2) correlated with the bond-strength data, and all fractures occurred within the adhesion zone: no ceramic fractures were noted. Groups that were not treated with an adhesive system (RCP, CP, and HF-control) presented mainly cohesive failures within the resin cement (C-RC) after 24 hours of water storage (Figures 2, 3a, 6a, and 7a). Moreover, 24-hour groups that were pretreated with an adhesive system (RCP+SB and SBU) presented mainly adhesive failures between the adhesive layer and the resin cement layer (AD-AC), showing an entire adhesive system layer adhering to the ceramic substrate. However, both layers morphology showed some differences between them (RCP+SB and SBU). The adhesive system layer from the RCP + SB group was seen to be uniform with the presence of some filler particles that were remnants from the resin cement layer (Figure 4a). Conversely, the SBU adhesive layer presented a very irregular pattern, showing some degree of discontinuity in the adhesive layer, with areas that apparently were not in contact with the resin cement and some that were before failure occurred (Figure 5a). After six months of storage,

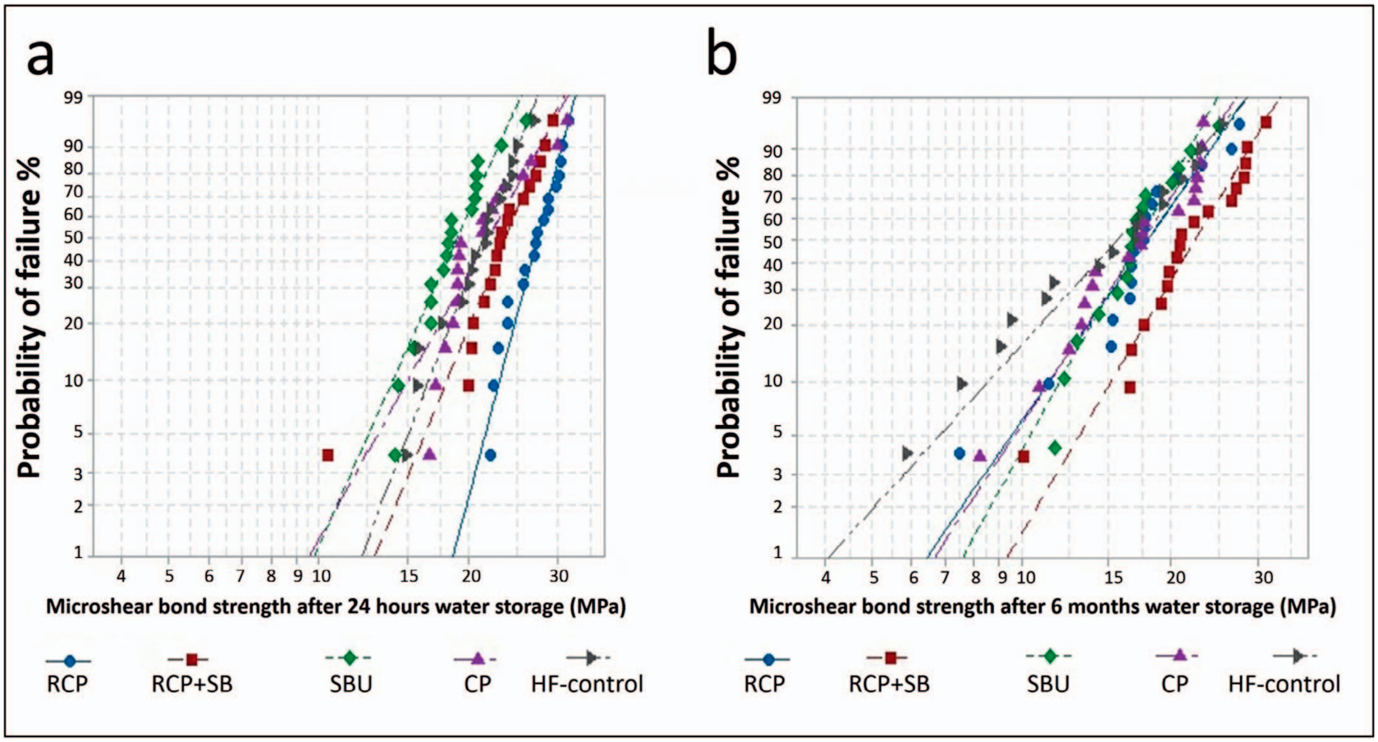

Figure 1. *Weibull distributions of microshear bond strength data related to water storage time at 37°C: (a) 24 hours and (b) six months. RCP, RelyX Ceramic Primer; RCP + SB, RelyX Ceramic Primer and Adper Single Bond 2; SBU, Single Bond Universal; CP, Clearfil Ceramic Primer; HF/control, no silane, 10% hydrofluoric acid treatment only. Lines drawn represent the Weibull curve shape.*

Table 3: *Weibull Modulus (m) and Weibull Characteristic Strength (σ_0) Values Among the Test Groups Stored for Either 24 Hours or Six Months in 37°C Water*

Ceramic Silane Treatment[a]	Storage Time (37°C Water)	N[b]	Number of Pretest Failures	Weibull Modulus (*m*)[c]	Weibull Modulus (95% Confidence Interval)[d]	Change in Weibull Modulus (and % With Storage)	Characteristic Strength (σ_0) (MPa)[e]	Characteristic Strength (95% Confidence Interval)[f]	Change in Characteristic Strength With Storage (MPa [%])
RCP	24 h	18	0	10.8	7.4-15.6	6.7 (61.8)	28.5	27.2-29.8	8.7 (30.7)
	6 mo	18	1	4.1	2.9-5.9		19.7	17.5-22.3	
RCP + SB	24 h	18	0	7.0	4.9-10.2*	2.2 (31.4)	24.9	23.3-26.7*	0.7 (2.7)
	6 mo	18	0	4.8	3.3-7.0*		24.3	22.0-26.9*	
SBU	24 h	18	0	6.4	4.6-8.9*	1.25 (19.5)	20.1	18.6-21.7*	1.5 (7,4)
	6 mo	18	2	5.1	3.6-7.4*		18.6	16.8-20.6*	
CP	24 h	18	0	5.1	3.7-7.1*	0.75 (14.7)	23.5	21.4-25.9*	4.3 (18.3)
	6 mo	18	0	4.3	3.0-6.4*		19.2	17.2-21.5*	
HF-control	24 h	18	0	7.5	5.2-10.8	4.37 (58.1)	22.5	21.1-24.0	4.8 (21.6)
	6 mo	18	1	3.1	2.1-4.6		17.6	15.0-20.7	

[a] *RCP, RelyX Ceramic Primer; RCP + SB, RelyX Ceramic Primer and Adper Single Bond 2; SBU, Single Bond Universal; CP, Clearfil Ceramic Primer; HF/control, no silane, 10% hydrofluoric acid only.*
[b] *Sample size.*
[c] *Determines how vertical the data distribution line is and infers how reliable the bond strength is. The higher the Weibull shape number (modulus, m), the more vertical the graph and the more reliable the treatment.*
[d] *Confidence intervals with an asterisk for each treatment are not significantly different, as they overlap.*
[e] *Determines the characteristic bond strength at a 63.2% failure probability. The higher the characteristic strength, the higher the bonding effectiveness.*
[f] *Confidence intervals with an asterisk for each treatment are not significantly different, as they overlap.*

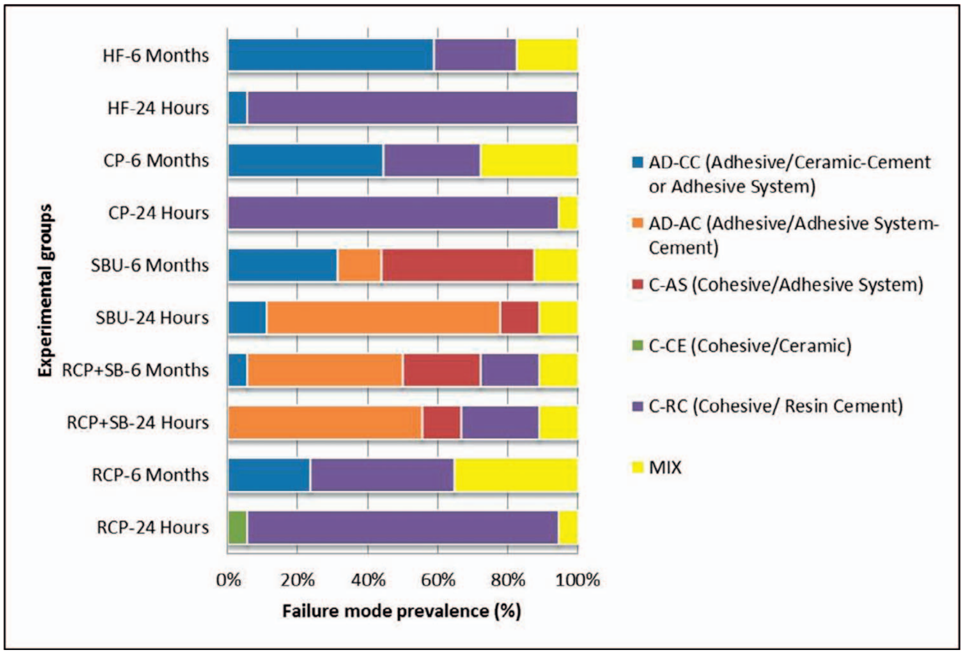

Figure 2. *Characterization of bond failure analysis from SEM images. RCP, RelyX Ceramic Primer; RCP + SB, RelyX Ceramic Primer and Adper Single Bond 2; SBU, Single Bond Universal; CP, Clearfil Ceramic Primer; HF/control, no silane, 10% hydrofluoric acid only.*

increased prevalences of adhesive failures between the resin cement or adhesive system and ceramic (AD-CC) and mixed failure patterns (MIX) were detected in the CP and HF-control groups, with more frequency of AD-CC failures for both (Figures 2, 6b, and 7b). In the case of RCP, a higher prevalence of AD-CC and MIX failure patterns was observed after six months of water storage, but a slightly higher prevalence of the C-RC type of failure was noted as a more irregular pattern than was observed after 24

Fig 3

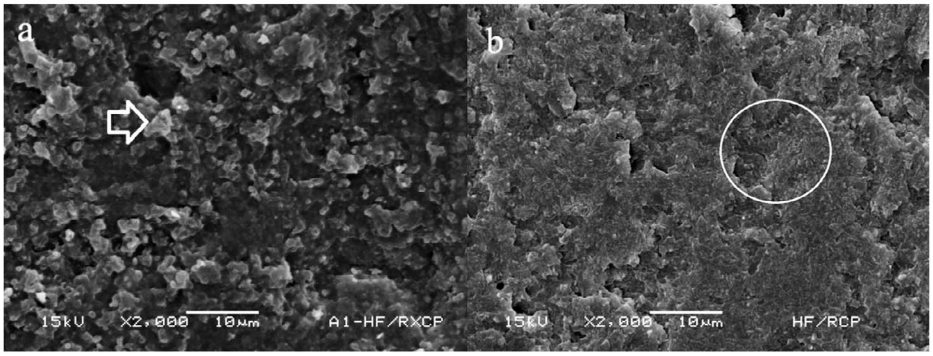

Figure 3. *Representative SEM micrographs of the more prevalent failure patterns observed in group RCP: (a) after 24 hours of water storage, where a C-RC failure can be seen along with the presence of resin cement filler particles (arrow), and (b) after six months of water storage, also showing a C-RC failure presenting an irregular/worn pattern within the surface (circle) in addition to showing fewer filler particles, as shown in Figure 3a.*

Fig 4

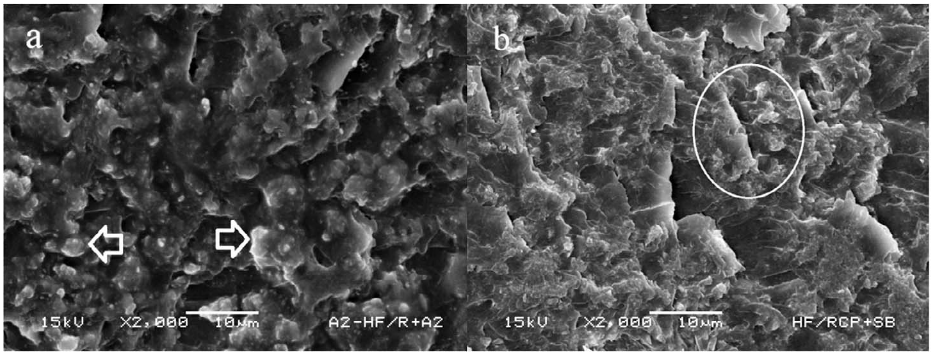

Figure 4. *Representative SEM micrographs of the more prevalent failure patterns observed in group RCP + SB: (a) after 24 hours of water storage, where an AD-AC failure is seen showing a regular adhesive layer with a few resin cement filler particles embedded within (arrow), and (b) after six months of water storage, also showing an AD-AC failure presenting an irregular/ worn pattern within the surface (circle) but this time showing almost no filler particles embedded on the adhesive layer.*

Fig 5

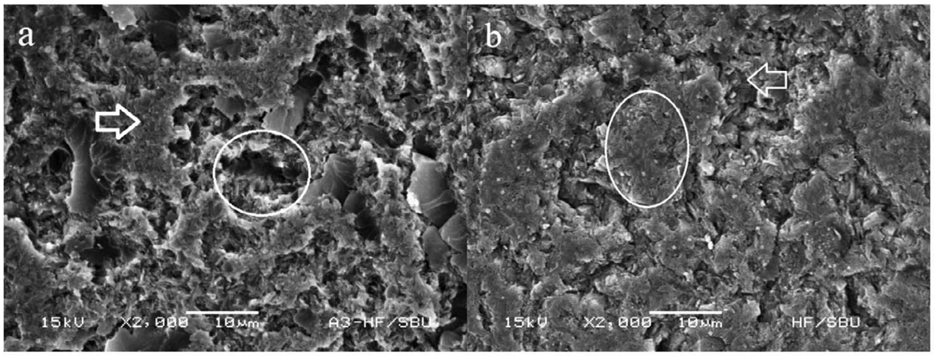

Fig 6

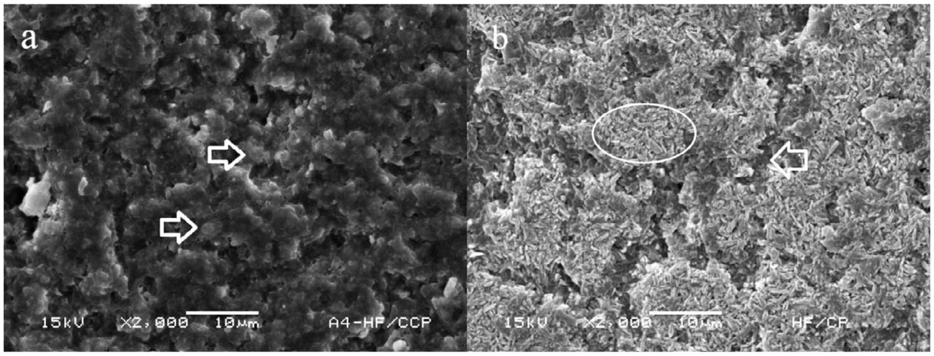

Fig 7

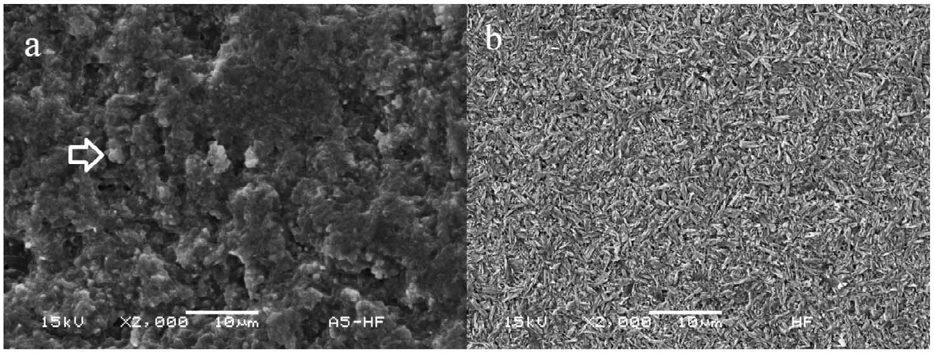

Figure 5. *Representative SEM micrographs of the more prevalent failure patterns observed in group SBU: (a) after 24 hours of water storage, where an AD-AC failure is seen showing a discontinuous and irregular adhesive layer formed by some areas of apparent deficient contact with the resin cement (circle) and some other areas that seem to have contacted the resin cement at the moment when failure occurred (arrow), and (b) after six months of water storage, showing a C-AS failure but very close to the ceramic surface, where a mixture of regions is noted, some with a thin layer of adhesive covering the ceramic surface (circle) and other areas with ceramic crystals exposed (arrow).*

Figure 6. *Representative SEM micrographs of the more prevalent failure patterns observed in group CP: (a) after 24 hours of water storage, where a C-RC failure is seen showing a continuous resin cement layer with some filler particles embedded (arrows), and (b) after six months of water storage, showing an AD-CC failure, with the ceramic surface and crystals exposed (circle) as well as some depressions caused by the airborne particle abrasion (arrow), producing an irregular pattern.*

Figure 7. *Representative SEM micrographs of the more prevalent failure patterns observed in the HF-only group (control): (a) after 24 hours of water storage, where a C-RC failure is seen, showing a continuous resin cement layer with some filler particles embedded (arrows), and (b) after six months of water storage, showing an AD-CC failure, where a regular layer formed by ceramic (lithium disilicate) crystals is noted. In this case, no depressions from airborne particle abrasion are seen, as in Figure 6b; instead, a completely uniform crystal surface is evident.*

hours of aging (Figures 2 and 3a,b). For the RCP + SB group, failure pattern prevalence was very similar after 24 hours or six months of aging, with more prevalence of other failure types after six months of storage but still demonstrating the AD-AC failure pattern most frequently (Figure 2). Furthermore, the adhesive layer morphology after six months was more irregular, and no resin cement remnant remained embedded in the adhesive layer, different from the pattern noted at 24 hours of storage (Figure 4a,b). More variation among failure patterns were noted for SBU after six months (Figure 2), being predominantly cohesive failure of the adhesive system (C-AS). This pattern was demonstrated by a thin, discontinuous adhesive layer, very close to the ceramic surface, where even some regions of underlying ceramic could be observed (Figure 5b). This observation indicates that, apparently, only a small portion of the adhesive layer remained attached to the ceramic surface for this bonding condition.

DISCUSSION

The results of this *in vitro* study show that the various silane treatments employed significantly influenced the ceramic/resin cement bond strength results, and thus the first null hypothesis was rejected. Because water aging also affected the bonding performance of resin cement to the glass ceramic, the second null hypothesis was also rejected. Thus, it can be said that variations in chemical formulations of commercial silane primers have a significant effect on their effectiveness as ceramic/resin cement bonding promoters. Because a significant interaction between factors (material and storage time) was detected, the specific effectiveness of bond strength was found to be product and treatment specific. In general, RCP and RCP + SB obtained the best results, while SBU and CP did not improve ceramic/resin cement bonding when compared to the use of only HF (Table 2).

The lower bond strengths obtained by SBU and CP, compared with the conventional silane (RCP) after 24 hours of storage, are in accordance with previous work.[20,21] Kalavacharla and others[20] found that SBU required initial application of a separate silane layer to improve adhesion between resin composite and lithium disilicate ceramic after 24 hours of water storage and thermocycling (10,000 cycles). Conversely, Kim and others[21] concluded that two universal adhesives did improve glass-ceramic/resin cement bonding when compared with a negative control group (only 9.5% HF alone); however, a separate application of silane followed by an adhesive showed better results. Those findings are similar with the data obtained in the present work after 24 hours of storage. One possible explanation is that, as SBU (pH 2.7) and CP (pH 3) are more acidic than the conventional silane (RCP, pH 4.6),[2] the silane contained in both SBU and CP may have been continuously hydrolyzed and reacting during storage and consequently been inactivated to some degree before being used. Additional influences may have affected the performance of SBU and CP, such as the addition of ingredients other than silane (mainly in the universal adhesive), resulting in less silane quantity per area of bonded substrate[22] in contact with the ceramic surface in contrast to the primer containing silane only. Intimate contact between silane and the ceramic surface is fundamental because with one silane coat, three oligomer layers are formed on the surface[23] and only the first layer is capable of forming chemical adhesion to the glass; the outermost layers may be detrimental.[24]

Also, elimination of solvents and other by-products formed during the silane condensation reaction may be hindered through the development of a dense polysiloxane polymer network.[25] A previous study showed that increased time to evaporate solvent in universal adhesives is needed (from the manufacturer-recommended 5 seconds to a longer time of 25 seconds) to improve its performance.[26]

The above assumption appears to be confirmed from evidence presented in the SEM images. In the SBU 24-hour group, some discontinuity areas (probably due to deficient solvent elimination) were observed, pointing to an incomplete, intimate contact with resin cement at the moment of polymerization (Figure 5a). Failure to form these bonds leads to stress concentration areas and a lowering of adhesive/resin cement adhesion, which may be consistent with the greater prevalence of AD-AC failure type obtained for this group (Figure 2). A similar pattern was previously reported for the same materials: RelyX Ultimate with Scotchbond Universal using feldspathic-ceramic[27] and CAD/CAM composite blocks (LAVA Ultimate, 3M ESPE).[28] In those papers, the authors infer that the observed voids are possibly the consequence of water in-flow from wet dentin tubules, probably due to undercured areas in the adhesive system/resin-cement assembly when the materials were not cured separately (adhesive and resin cement).[27,28] In the present work, dentin was not used, and it is more appropriate to consider that water or humidity arose from the silane/ceramic condensation reaction or the incompletely eliminated solvent. Moreover, for the groups RCP, CP, and HF, mostly cohesive failure within the resin cement (C-RC) was noted after 24 hours of storage (Figures 2, 3a, 6a, and 7a). This failure type is associated with higher bond strength values in accordance with previous work.[18,25,29,30]

After six months of water aging, a different scenario was observed. RCP and the HF-control showed a significant drop in bond strength compared to their 24-hour values (Table 2). Conversely, groups RCP + SB (highest mean), SBU, and CP still provided more consistent bond strength values between 24 hours and six months of water storage, with RCP + SB demonstrating the least effect of water storage (only 5%) (Table 2). Consistently, failure pattern prevalence of the RCP + SB group remained almost the same between 24 hours and six months (Figure 2). In the case of SBU, water degradation may have reduced the cohesive strength of the adhesive layer, indicating that the fracture may have occurred very close to the adhesive/ceramic interface (Figure 5). Even though SBU bond strength also decreased with water storage, it could be assumed that the presence of its hydrophobic monomers prevented, to some degree, a fully adhesive failure between ceramic and the adhesive, as happened with the CP and HF-control groups.

The better performance exhibited by RCP + SB and SBU against water aging may be due to the presence of hydrophobic monomers and MDP, which may better resist hydrolytic degradation because of their chemical nature. On the other hand, groups using a conventional silane (RCP) and HF-only treatment alone (HF-control) show no such protection against hydrolytic degradation: a 34% and a 26% decrease in bond strength with storage time, respectively. Such findings are supported by SEM failure analysis where those groups exhibited increased adhesive failure-type prevalence (AD-CC) and some other signs of hydrolytic effects, such as less resin cement particle presence (Figures 2 and 3) or even exposed lithium disilicate crystals (Figures 2 and 7).

Weibull analysis also showed a decrease in the reliability and characteristic bond strength for the RCP and HF-control groups after six months of water storage; for RCP + SB, SBU, and CP, no such decrease was detected (Figure 1; Table 3). These results indicate that, although all groups exhibited higher Weibull parameters at 24 hours of water storage than after six months, groups RCP + SB and SBU were less affected by water aging (Figure 1; Table 3). This finding may support the theory that a mostly hydrophobic adhesive system, used in conjunction with a silane coupling agent, may better resist hydrolytic degradation of the siloxane network. Weibull analysis is a useful tool in associating bond strength with probability of failure. Previous studies used this type of analysis to evaluate dental materials strength,[31] ceramic/resin cement bond strength,[32,33] and zirconia/resin cement bonding.[34] Using this evaluation method, the present work demonstrated that RCP + SB and SBU provided the most reliable treatments in the long term (Figure 1; Table 3).

In terms of bond strength, RCP + SB performed better than SBU (Tables 2 and 3; Figure 1). This finding could be explained by the fact that when applying the silane and the adhesive separately, the full ceramic surface is first contacted by silane molecules, possibly causing a higher chemical interaction between silane and the ceramic. Consequently, evaporation of solvent and condensation reaction by-products may be more efficient using the separate silane application than when silane is mixed with other components, as also suggested by others.[21] This result suggests that an adhesive layer (preferably hydrophobic), placed subsequent to silane application, may be useful in delaying hydrolytic degradation of the siloxane network formed at the ceramic/resin cement interface in addition to other benefits, such as increasing resin cement wettability,[35-37] serving as a shock-absorbing layer,[38] and increasing bond stability[39] and bond strength between the glass ceramic and resin cement.[40]

The selection of products and treatments used in this investigation demonstrated different results related to water storage duration. Consequently, use of a silane coupling agent, together with a mostly hydrophobic adhesive system (applied separately), may be recommended for glass-ceramic pretreatment. Future investigations should evaluate the ceramic/resin cement bonding stability (mechanical and chemical analysis) produced by silane-containing universal adhesives and ceramic primers for longer time periods and among a more diverse group of ceramic substrates.

CONCLUSIONS

Within the limitations of this *in vitro* study, the following conclusions may be drawn:

1) Placement of conventional silane followed by an adhesive system application improved ceramic/resin cement bond strength after both short- and long-term water aging.
2) Application of separate silane and adhesive components and a silane-containing, universal adhesive demonstrated the least decrease in microshear bond strength after long-term water storage.
3) The conventional silane and the HF–only controls showed reduced bond strength from 24 hours to six months of water storage, while silane, followed by adhesive application, the universal adhesive, and the universal ceramic primer, did not change during that time period.

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Conflict of Interest

The authors of this article certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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REFERENCES

1. Peumans M, Van Meerbeek B, Lambrechts P, & Vanherle G (2000) Porcelain veneers: A review of literature *Journal of Dentistry* **28(3)** 163-177.
2. Ying Kei Lung C, & Matinlinna JP (2012) Aspects of silane coupling agents and surface conditioning in dentistry: An overview *Dental Materials* **28(5)** 467-477.

3. Peumans M, De Munck J, Van Landuyt KL, Poitevin A, Lambrechts P, & Van Meerbeek B (2010) Eight-year clinical evaluation of a 2-step self-etch adhesive with and without selective enamel etching *Dental Materials* **26(12)** 1176-1184.
4. Brentel SA, Özcan M, Valandro LF, Guimarães Alarça L Amaral R, & Bottino MA (2007) Microtensile bond strength of a resin cement to feldspathic ceramic after different etching and silanization regimens in dry and aged conditions *Dental Materials* **23(11)** 1323-1331.
5. Blatz MB, Dent M, Sadan A, & Kern M (2003) Resin-ceramic bonding: A review of the literature *Journal of Prosthetic Dentistry* **89(3)** 268-274.
6. Scherrer SS, de Rijk WG, Belser UC, & Meyer JM (1994) Effect of cement film thickness on the fracture resistance of a machinable glass-ceramic *Dental Materials* **10(3)** 172-177.
7. Fradeani M, & Redemagni M (2002) An 11-year clinical evaluation of leucite-reinforced glass-ceramic crowns: A retrospective study *Quintessence International* **33(7)** 503-510.
8. Chen JH, Matsumura H, & Atsuta M (1998) Effect of etchant, etching period, and silane priming on bond strength to porcelain of composite resin *Operative Dentistry* **23(5)** 250-257.
9. Addison O, Marquis PM, & Fleming GJ (2007) The impact of hydrofluoric acid surface treatments on the performance of a porcelain laminate restorative material *Dental Materials* **23(4)** 461-468.
10. Eames WB, Rogers LB, Feller PR, & Price WR (1977) Bonding agents for repairing porcelain and gold: An evaluation *Operative Dentistry* **2(3)** 118-124.
11. Matinlinna JP, Lassila LV, & Vallittu PK (2007) Pilot evaluation of resin composite cement adhesion to zirconia using a novel silane system *Acta Odontologica Scandinavica* **65(1)** 44-51.
12. Matinlinna JP, Lassila LV, Özcan M, Yli-Urpo A, & Vallittu PK (2004) An introduction to silanes and their clinical applications in dentistry *International Journal of Prosthodontics* **17(2)** 155-164.
13. Anagnostopoulos T, Eliades G, & Palaghias G (1993) Composition, reactivity and surface interaction of three dental silane primers *Dental Materials* **9(3)** 182-190.
14. Blatz MB, Sadan A, Martin J, & Lang B (2004) In vitro evaluation of shear bond strengths of resin to densely sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling *Journal of Prosthetic Dentistry* **91(4)** 356-362.
15. Kitayama S, Nikaido T, Takahashi R, Zhu L, Ikeda M, Foxton RM, Sadr A, & Tagami J (2010) Effect of primer treatment on bonding of resin cements to zirconia ceramic *Dental Materials* **26(5)** 426-432.
16. Van Meerbeek B, Yoshihara K, Yoshida Y, Mine A, De Munck J, & Van Landuyt KL (2011) State of the art of self-etch adhesives *Dental Materials* **27(1)** 17-28.
17. Van Meerbeek B, De Munck J, Yoshida Y, Inoue S, Vargas M, Vijay P, Van Landuyt K, Lambrechts P, & Vanherle G (2003) Buonocore memorial lecture: Adhesion to enamel and dentin: Current status and future challenges *Operative Dentistry* **28(3)** 215-235.
18. Borges GA, Spohr AM, de Goes MF, Sobrinho LC, & Chan DC (2003) Effect of etching and airborne particle abrasion on the microstructure of different dental ceramics *Journal of Prosthetic Dentistry* **89(5)** 479-488.
19. Shimada Y, Yamaguchi S, & Tagami J (2002) Micro-shear bond strength of dual-cured resin cement to glass ceramics *Dental Materials* **18(5)** 380-388.
20. Kalavacharla VK, Lawson NC, Ramp LC, & Burgess JO (2015) Influence of etching protocol and silane treatment with a universal adhesive on lithium disilicate bond strength *Operative Dentistry* **40(4)** 372-378.
21. Kim RJ, Woo JS, Lee IB, Yi YA, Hwang JY, & Seo DG (2015) Performance of universal adhesives on bonding to leucite-reinforced ceramic *Biomaterials Research* **19(11)** 1-6.
22. Ikemura K, Tanaka H, Fujii T, Deguchi M, Negoro N, Endo T, & Kadoma Y (2011) Design of a new, multi-purpose, light-curing adhesive comprising a silane coupling agent, acidic adhesive monomers and dithiooctanoate monomers for bonding to varied metal and dental ceramic materials *Dental Materials Journal* **30(4)** 493-500.
23. Ishida H, & Koenig JL (1980) A Fourier-transform infrared spectroscopic study of the hydrolytic stability of silane coupling agents on E-glass fibers *Journal of Polymer Science: Polymer Physics* **18(9)** 1931-1943.
24. Berg J, & Jones FR (1998) The role of sizing resins, coupling agents and their blends on the formation of the interphase in glass fiber composites *Composites Part A: Applied Science and Manufacturing* **29(9-10)** 1261-1272.
25. Shen C, Oh WS, & Williams JR (2004) Effect of post-silanization drying on the bond strength of composite to ceramic *Journal Prosthetic Dentistry* **91(5)** 453-458.
26. Luque-Martinez IV, Perdigão J, Muñoz MA, Sezinando A, Reis A, & Loguercio AD 2014 Effects of solvent evaporation time on immediate adhesive properties of universal adhesives to dentin *Dental Materials* **30(10)** 1126-1135.
27. Lührs AK, De Munck J, Geurtsen W, & Van Meerbeek B (2014) Composite cements benefit from light-curing *Dental Materials* **30(3)** 292-300.
28. Lührs AK, Pongprueska P, De Munck J, Geurtsen W, & Van Meerbeek B. Curing mode affects bond strength of adhesively luted composite CAD/CAM restorations to dentin *Dental Materials* **30(3)** 281-291.
29. Pollington S, Fabianelli A, & Van Noort R (2010) Microtensile bond strength of a resin cement to a novel fluorcanasite glass-ceramic following different surface treatments *Dental Materials* **26(9)** 864-872.
30. Hooshmand T, Van Noort R, & Keshvad A (2004) Storage effect of a pre-activated silane on the resin to ceramic bond *Dental Materials* **20(7)** 635-642.

31. Quinn JB, & Quinn GD (2010) A practical and systematic review of Weibull statistics for reporting strengths of dental materials *Dental Materials* **26(2)** 135-147.
32. Della Bona A, Anusavice KJ, & Mecholsky JJ Jr (2003) Failure analysis of resin composite bonded to ceramic *Dental Materials* **19(8)** 693-699.
33. Della Bona A, Anusavice KJ, & Mecholsky JJ Jr (2006) Apparent interfacial fracture toughness of resin/ceramic systems *Journal of Dental Research* **85(11)** 1037-1041.
34. Inokoshi M, Poitevin A, De Munck J, Minakuchi S, & Van Meerbeek B (2014) Bonding effectiveness to different chemically pre-treated dental zirconia *Clinical Oral Investigations* **18(7)** 1803-1812.
35. Hooshmand T, van Noort R, & Keshvad A (2002) Bond durability of the resin bonded and silane treated ceramic surface *Dental Materials* **18(2)** 179-188.
36. Addison O, Marquis PM, & Fleming GJ (2007) Resin strengthening of dental ceramics-the impact of surface texture and silane *Journal of Dentistry* 2007 **35(5)** 416-424.
37. Sundfeld Neto D, Naves LZ, Costa AR, Correr AB, Consani S, Borges GA, & Correr-Sobrinho L (2015) The effect of hydrofluoric acid concentration on the bond strength and morphology of the surface and interface of glass ceramics to a resin cement *Operative Dentistry* **40(5)** 470-479.
38. Lastumaki TM, Lassila LV, & Vallittu PK (2003) The semi-interpenetrating polymer network matrix of fiber-reinforced composite and its effect on the surface adhesive properties *Journal of Materials Science: Materials in Medicine* **14(19)** 803-809.
39. El Zohairy AA, De Gee AJ, Hassan FM, & Feilzer AJ (2004) The effect of adhesives with various degrees of hydrophilicity on resin ceramic bond durability *Dental Materials* **20(8)** 778-787.
40. Naves LZ, Soares CJ, Moraes RR, Gonçalves LS, Sinhoreti MA, & Correr-Sobrinho L (2010) Surface/interface morphology and bond strength to glass ceramic etched for different periods *Operative Dentistry* **35(4)** 420-427.