Effect of MDP-containing Silane and Adhesive Used Alone or in Combination on the Long-term Bond Strength and Chemical Interaction with Lithium Disilicate Ceramics

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Purpose: To evaluate the effect of a silane and an adhesive containing MDP, used alone or combined in the same solution, on the microshear bond strength (μSBS) to lithium disilicate ceramics immediately and after 1-year water storage, and compare the bond strength results with the Raman spectra of the treated lithium disilicate surfaces.

Materials and Methods: A total of 30 CAD/CAM blocks of lithium disilicate (LD; IPS e.max CAD) were cut into four square sections (6 x 6 x 6 mm; n = 60 per group) and processed as recommended by the manufacturer. The LD specimens were divided into 12 groups according to the following independent variables: silane coupling agent (no silane; silane without 10-MDP [MBS, Monobond S]; silane with 10-MDP [MB+, Monobond Plus]) and adhesive + luting composite (no adhesive + Enforce; no adhesive + RelyX Ultimate; Prime & Bond Elect [PBE], a silane- and MDP-free universal adhesive + Enforce; Scotchbond Universal Adhesive [SBU], a silane- and MDP-containing universal adhesive + RelyX Ultimate). After each treatment, cylindrical, transparent matrices were filled with a luting composite and light cured. Specimens were stored in water (37°C for 24 h or 1 year) and submitted to the microshear bond strength (μSBS) test. The failure pattern and μSBS were statistically evaluated (α = 0.05). In addition, specimens were examined for chemical interaction using Raman spectroscopy.

Results: The use of the adhesive PBE alone showed higher mean μSBS compared with both groups with silane (MSB or MB+) without PBE ($p < 0.001$) at 24 h. The use of the SBU adhesive or MBS silane alone, as well as MB+ associated with SBU, showed higher mean μSBS ($p < 0.001$) at 24 h. After 1-year water storage, all groups showed a significant decrease in mean μSBS. However, the application of PBE or SBU associated with MB+ silane showed higher 1-year mean μSBS ($p < 0.001$). In terms of chemical interaction, when silane (MSB or MB+) was applied, only a slight decrease of Si-O peaks occurred. Otherwise, when PBE or SBU adhesives were applied, methacrylate peaks were only observed in the SBU groups.

Conclusion: The best results in terms of bond strength after water storage were obtained when an MDP-containing silane was associated with a universal adhesive. The use of a simplified bonding protocol that includes either a silane or a universal adhesive is not recommended.

Keywords: luting composite, resin cement, universal dentin adhesive, CAD/CAM lithium disilicate, bond strength.

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Dental ceramic restorations have become popular because of their clinical performance, long-term esthetics, and excellent biocompatibility.[4,5,58] The development of leucite- and lithium disilicate-reinforced glass-matrix synthetic ceramics, aimed at improving the strength over that of feldspathic dental ceramics, made it possible to expand the clinical indications to posterior teeth, as well as increase the durability of ceramic restorations.[20,25]

One key to the success of ceramic restorations is the optimization of the bonding procedure between the ceramics and the dental tissue.[26,55] The ceramic intaglio surface must be etched with hydrofluoric acid (HF) prior to adhesive cementation to enamel and dentin surfaces.[55] HF etching results in the dissolution of glassy phases of ceramics, consequently increasing roughness and the surface area for bonding.[7,9,46,49,55] Studies have shown that HF etching of lithium disilcate (LD) improves bond strengths.[21,23,41] The traditional bonding protocol for glass-matrix ceramics also requires a silane coupling agent to provide chemical bonding.[17,60] In fact, bond strengths increase when a silane coupling agent is applied.[23] The application of a silane coupling agent onto the etched intaglio surface promotes a bifunctional adhesion mechanism, creating a chemical interaction/adsorption between the silica in the glassy phase of the ceramics and the methacrylate groups of the luting resin through siloxane bonds.[31,36,56] Additionally, there is an increase in surface energy and wettability after etching and silanization, which results in a decrease of the contact angle between the ceramics and luting composite.[47]

Functional monomers, such as 10-MDP (MDP), have been added to the composition of silane solutions in order to increase the potential for chemical interaction. Current examples are Clearfil Ceramic Primer (Kuraray Noritake; Tokyo, Japan) and Monobond Plus (MB+, Ivoclar Vivadent; Schaan, Liechtenstein). Theoretically, a silane coupling agent containing MDP, such as MB+, might improve the chemical interaction with different ceramic surfaces. Therefore, these silane-MDP solutions could be used simultaneously as zirconia and lithium disilicate primers. The application of MB+ on the LD intaglio surface is currently recommended in the dual role of silane and adhesive by the respective manufacturer. This simplification makes the clinical bonding procedure more user friendly than having to apply a silane solution and an adhesive separately.

Universal adhesives were recently introduced.[22,39,44,45] Although the universal adhesive concept was advocated many years ago,[57] more recently, different authors have expanded this idea by using the same universal adhesive on several substrates, including composite, ceramics, zirconia, and metal alloys without the need for additional primers.[6,28,53] Most universal adhesives contain functional monomers, such as MDP, which improves the chemical bonding to different substrates.[8,40,61,63]

Another recent development in dental adhesion is the introduction of silane-containing universal adhesives, specifically Clearfil Universal Bond (Kuraray Noritake) and Scotchbond Universal Adhesive (3M ESPE; St Paul, MN, USA). Although the clinical use of a universal adhesive with silane in the same solution is very convenient to bond glass-matrix ceramics, the combination of silane and resin monomers in universal adhesives is controversial.[10,23] Water contact-angle measurements and bond strength testing have demonstrated that a silane may be incompatible with methacrylate monomers when mixed in the same solution.[10,64] Additionally, the application of Scotchbond Universal Adhesive to LD etched with 5% HF for 20 s resulted in lower bond strengths than the application of a separate silane solution followed by the same universal adhesive.[23]

Although some of the universal adhesives currently available contain functional monomers other than MDP, the efficacy of silane-containing universal adhesives with or without MDP has not been thoroughly investigated. Thus, the aim of this study was to evaluate the effect of silane with or without MDP and the effect of universal adhesives combined or not with silane on the immediate and long-term bonding efficacy of luting composites (also known as resin cements) to LD glass ceramics using microshear bond strength testing and Raman spectroscopy.

The null hypotheses were: 1) A silane containing MDP does not enhance adhesion when compared to an MDP-free silane; 2) a universal adhesive containing MDP does not improve adhesion compared to an MDP-free universal adhesive; 3) the application of a silane and a universal adhesive, separately or combined in the same solution, does not result in improved adhesive properties compared to the use of a separate silane or a separate universal adhesive; 4) 1-year water storage does not result in worse adhesion for any of the combination of adhesives and silanes.

MATERIALS AND METHODS

Specimen Preparation

A total of 30 CAD/CAM blocks (12 x 12 x 6 mm) of LD (IPS e.max CAD; Ivoclar Vivadent) were used. Each block was cut into four square sections (6 x 6 x 6 mm; n = 120) using a diamond disk in a low-speed saw (Isomet, Buehler; Lake Bluff, IL, USA) under water cooling. After ultrasonic cleaning in distilled water for 15 min, the ceramic specimens were fired following the crystallization program in a furnace (Programat P300, Ivoclar Vivadent) at 840°C to 850°C for 20–31 min.

Experimental Design

The LD specimens were randomly assigned (http://www.sealedenvelope.com) to 12 experimental conditions (n = 10), with 96 specimens for microshear bond strength (μSBS) testing to evaluate the bond strength and 24 specimens for Raman spectroscopy to evaluate the chemical interaction of silane agents and adhesives with LD. The experimental groups were formed according to the following independent variables: silane coupling agent (no silane; silane without MDP [MBS, Monobond S, Ivoclar Vivadent]; silane with MDP [MB+, Monobond Plus Ivoclar Vivadent])

Table 1 Materials used, batch numbers, compositions and application mode

Material, manufacturer (batch number)	Composition	Application mode
Monobond S – MBS Ivoclar Vivadent (R26558)	1% 3-methacryloxypropyl trimethoxysilane, ethanol/water-based solvent, acetic acid	1. Apply with a brush and let react for 60 s. 2. Apply strong stream of air to ensure solvent evaporation.
Monobond Plus – MB+ Ivoclar Vivadent (S31153)	Ethanol, 3-trimethoxysilylpropyl methacrylate, 10-MDP(MDP), sulphide methacrylate	1. Apply with a brush and let react for 60 s. 2. Apply strong stream of air to ensure solvent evaporation.
Prime & Bond Elect – PBE Dentsply (130811)	Adhesive: mono-, di- and trimethacrylate resins, PENTA diketone, organic phosphine oxide, stabilizers, cetylamine hydrofluoride, acetone, water Self-curing activator: mono- and di-methacrylate resins, catalyst, photoinitiators, stabilizers, acetone, water	1. Mix one drop each of adhesive and self-curing activator. 2. Apply a generous amount of adhesive/activator to thoroughly wet all surfaces and leave undisturbed for 20 s. 3. Gently dry with clean air for at least 5 s. 4. Light cure adhesive/activator for 10 s.
Scotchbond Universal Adhesive – SBU 3M ESPE (523652)	10-MDP (MDP) phosphate monomer, dimethacrylate resins, HEMA, methacrylate-modified polyalkenoic acid copolymer, filler, ethanol, water, initiators, silane	1. Apply the adhesive and leave undisturbed for 20 s. 2. Direct a gentle stream of air over the liquid for about 5 s until it no longer moves and the solvent is evaporated completely.
Enforce Dentsply	Base: bis-GMA, TEG-DMA, camphorquinone , EDAB, BHT, DHEPT Catalyst: bis-GMA, BHT, EDAB, TEG-DMA, benzoylperoxide	1. Mix the two pastes at a 1:1 ratio. 2. Light cure for 30 s.
RelyX Ultimate 3M ESPE	Base: silane-treated glass powder, 2-propenoic acid, 2-methyl-,1,1-[1-(hydroxymethyl)-1,2-ethanediyl] ester, reaction products with 2-hydroxy-1,3-propanediyl DMA and phosphorus oxide, TEG-DMA, silane treated silica, oxide glass chemicals, sodium persulfate, tert-butyl peroxy-3,5,5-trimethylhexanoate, copper (II) acetate monohydrate Catalyst: silane-treated glass powder, substituted DMA, 1,12-dodecane DMA, silane treated silica, 1-benzyl-5-phenyl-barbic-acid, calcium salt, sodium p-toluenesulfinate, 2-propenoic acid, 2-methyl-, [(3-metoxypropyl) imino]di-2,1-ethanediyl ester, calcium hydroxide, titanium dioxide	1. Mix the two pastes in the automix syringe using a standard mixing tip. 2. Light cure for 20 s.

MDP: 10-methacryloyloxydecyl dihydrogen phosphate; BHT: butylhydroxytoluene; HEMA: hydroxyethyl methacrylate; bis-GMA: bisphenol-A glycidyl dimethacrylate; DHEPT: N,N-di-(2-hydroxyethyl)-4-toluidine; EDAB: ethyl 4-dimethylamine b; PENTA: dipentaerythritol penta acrylate monophosphate; TEG-DMA: triethylene glycol dimethacrylate.

and adhesive + luting composite (no adhesive + Enforce [Dentsply Caulk; Milford, DE, USA]; no adhesive + RelyX Ultimate [3M ESPE]; Prime & Bond Elect [PBE], a silane- and MDP-free universal adhesive + Enforce [Dentsply Caulk]; Scotchbond Universal Adhesive [SBU], a silane- and MDP-containing universal adhesive + RelyX Ultimate [3M ESPE]). The composition, application mode, and batch numbers are described in Table 1.

Microshear Bond Strength (μSBS)

All LD specimens were mounted in a polyvinyl chloride (PVC) ring filled with acrylic resin (AutoClear, DentBras; Pirassununga, São Paulo, Brazil), leaving the specimen surface at a height of 3 mm on the top of the cylinder. The specimens were etched with 5% HF acid (Condac Porcelain Etch 5%, FGM; Joinville, SC, Brazil) for 20 s, thoroughly rinsed with water spray for 30 s, and ultrasonically cleaned in distilled water for 180 s. The silane coupling agent and adhesive were then applied according to the respective manufacturer's instructions (Table 1). A single operator performed all bonding procedures.

After the application of the adhesive, seven transparent polyethylene Tygon tubes (Tygon Medical Tubing Formulations 54-HL, Saint Gobain Performance Plastics; Akron, OH, USA) with an internal diameter of 0.8 mm and a height of 0.5 mm were positioned over the LD surface of each specimen. The luting composite (Table 1) was carefully packed inside each tube, then a clear Mylar matrix strip was placed over the filled Tygon tube and pressed gently into place. The luting composite specimens were simultaneously light cured for 20 s using an LED light-curing unit set at 1200 mW/cm^2 (Radii-cal, SDI; Bayswater, Victoria, Austra-

lia). A radiometer (Demetron L.E.D. Radiometer, Kerr Sybron Dental Specialties; Middleton, WI, USA) was used to check the light intensity every five luting composite cylinders. These procedures were carried out under magnifying loupes.[38]

After storage of the specimens in distilled water for 24 h at 37°C, the Tygon tubes were carefully removed with a blade to expose the cement cylinders. Each specimen was examined under a stereomicroscope at 10X magnification. The cement cylinder was discarded if there was evidence of porosity or gaps at the interface.

Half of the specimens of each experimental group were stored in water at 37°C for 1 year. The other half was tested after 24 h. The specimens were attached to a shear-testing fixture (Odeme Biotechnology; Joaçaba, SC, Brazil) and tested in a universal testing machine (Kratos IKCL 3-USB, Kratos Equipamentos Industriais; Cotia, São Paulo, Brazil). Each specimen was positioned on the universal testing machine and a thin orthodontic wire (0.2 mm diameter) was looped around the base of each composite cylinder. The orthodontic wire contacted the composite cement cylinder along half of its circumference. The assembly was kept aligned (cement-ceramics interface, the wire loop, and the center of the load cell) to ensure correct orientation of the shear forces.[54] The crosshead speed was set at 1 mm/min until failure.

The μSBS values (MPa) were calculated by dividing the load at failure by the surface area (mm^2). After testing, the specimens were examined under an optical microscope (SZH-131, Olympus; Tokyo, Japan) at 100X magnification to define the location of the bond failure. The failure mode was classified as cohesive in luting composite ([CLC] failure exclusively within the resin cement), cohesive in ceramic ([CC] failure exclusively within ceramic), adhesive/mixed ([A/M] failure at the cement-ceramics interface that included cohesive failure of the neighboring substrates).

Chemical Interaction Analysis by Raman Spectroscopy

Two LD specimens were analyzed per experimental treatment group. A Raman spectrometer (Horiba Scientific; Tokyo, Japan) was first calibrated for zero and then for coefficient values using a silicon specimen. Specimens were analyzed using the following Raman parameters: 20 mW HeNe laser with 632.8 nm wavelength, spatial resolution of ≈ 3 μm, spectral resolution ≈ 5 cm^{-1}, accumulation time of 300 s, with 2 co-additions, and magnification of 100X (Olympus UK; London, UK), and a beam diameter of 1 μm in a range 900 to 1850 cm^{-1}. First, spectra were taken of silane coupling agent, uncured adhesives, and ceramic surface separately. Then each silane coupling agent and adhesive were applied according the manufacturer's instructions. The specimens were subsequently rinsed for 1 min in distilled water (30 s) and absolute ethanol (30 s), as described by Yoshihara et al.[65] The spectra were obtained in triplicate and a comparison was carried out by spectra subtraction for qualitative analysis.

Statistical Analysis

Before submitting the data to the appropriate statistical test, they were checked for normal distribution with the Kolmogorov-Smirnov test; Barlett's test was performed to determine if the assumption of equal variances was valid.[37] After confirming normal distribution and the equality of variances of the data, the μSBS of all specimens from the same individual LD specimens were averaged for statistical purposes. The μSBS data were analyzed using two-way ANOVA (groups vs time) for each adhesive used. Tukey's post-hoc test was applied with $\alpha = 0.05$. For pairwise comparison between adhesives (PBE and SBU) in the same experimental situation, Student's t-test for independent samples was applied ($\alpha = 0.05$).

RESULTS

Microshear Bond Strength (μSBS)

Fifty-six bonded cylinders were tested for each experimental group. No specimens were discarded due to porosities or other defects, nor were any pre-test failures observed. The majority of specimens showed adhesive/mixed failures after 24-h and 1-year water storage (Table 2).

Enforce resulted in the lowest 24-h mean μSBS (Tukey's test; $p < 0.05$; Table 3) when no adhesive or silane were used. The use of the adhesive PBE without silane resulted in statistically significantly higher 24-h mean μSBS compared with both groups with silane without PBE (MSB or MB+) (Tukey's test; $p < 0.05$; Table 3). The application of PBE associated with a silane (MSB or MB+) showed intermediate 24-h mean μSBS. After 1 year of water storage, all groups showed a significant decrease in mean μSBS (Tukey's test; $p < 0.05$; Table 3). However, the application of luting composite without any adhesive showed the lowest 1-year mean μSBS, while the application of PBE associated with a MB+ silane showed the highest 1-year mean μSBS (Tukey's test; $p < 0.05$; Table 3).

RelyX Ultimate resulted in statistically significantly higher 24-h mean μSBS (Tukey's test; $p < 0.05$; Table 4) when SBU adhesive or MBS silane were used alone, and when MB+ was associated with SBU. However, the association of either MBS or MB+ with SBU, as well as MB+ without any adhesive, resulted in similar immediate μSBS for the luting composite group only (Tukey's test; $p < 0.05$; Table 4). After 1 year of water storage, all groups showed a significant decrease of mean μSBS ($p < 0.001$; Table 3). However, the application of luting composite without any adhesive showed the lowest 1-year mean μSBS, while the application of SBU associated with MB+ showed the highest 1-year mean μSBS (Tukey's test; $p < 0.05$; Table 4).

PBE resulted in statistically significantly higher 24-h mean μSBS in all groups when compared with SBU (Tukey's test; $p < 0.05$; Table 5). However, after 1 year of water storage, all groups of both adhesives showed similar mean μSBS ($p > 0.05$; Table 5), with the exception of PBE associated with MB+, which showed higher mean μSBS than SBU associated with MB+ (Tukey's test; $p > 0.05$; Table 5).

Table 2 Number (%) of specimens according to fracture mode

Luting composite Enforce*	Fracture mode					
	Immediate			1-year		
	A/M	CLC	CC	A/M	CLC	CC
No adhesive/no silane	14 (50)	14 (50)	0 (0)	21 (75)	7 (25)	0 (0)
Adhesive	26 (93)	2 (07)	0 (0)	24 (86)	4 (14)	0 (0)
Silane without MDP (MBS)	22 (79)	6 (21)	0 (0)	24 (86)	4 (14)	0 (0)
Silane without MDP (MBS) + adhesive	20 (71)	8 (29)	0 (0)	25 (89)	3 (21)	0 (0)
Silane with MDP (MB+)	24 (86)	4 (14)	0 (0)	23 (82)	5 (18)	0 (0)
Silane with MDP (MB+) + adhesive	20 (71)	8 (29)	0 (0)	28 (100)	0 (0)	0 (0)
Luting composite RelyX Ultimate**	Fracture mode					
	Immediate			1-year		
	A/M	CLC	CC	A/M	CLC	CC
No adhesive/no silane	20 (71)	8 (29)	0 (0)	23 (82)	5 (18)	0 (0)
Adhesive	27 (96)	1 (04)	0 (0)	26 (93)	2 (07)	0 (0)
Silane without MDP (MBS)	23 (82)	5 (18)	0 (0)	25 (89)	3 (21)	0 (0)
Silane without MDP (MBS) + adhesive	23 (82)	5 (18)	0 (0)	26 (93)	2 (07)	0 (0)
Silane with MDP (MB+)	25 (89)	3 (21)	0 (0)	24 (86)	4 (14)	0 (0)
Silane with MDP (MB+) + adhesive	24 (86)	4 (14)	0 (0)	28 (100)	0 (0)	0 (0)

*Prime & Bond Elect was used with Enforce. MBS: Monobond S; MB+: Monobond Plus. **Scotchbond Universal Adhesive was used with RelyX Ultimate. A/M: adhesive/mixed; CLC: cohesive in luting cement; CC: cohesive in ceramic.

Table 3 Mean bond strengths (MPa) of Enforce to lithium disilicate

	No adhesive/ no silane	Adhesive*	Silane without MDP (MBS)	Silane without MDP (MBS) + adhesive*	Silane with MDP (MB+)	Silane with MDP (MB+) + adhesive*
Immediate	27.1 ± 1.7^{C}	32.1 ± 1.7^{A}	29.9 ± 2.8^{B}	30.0 ± 0.9^{A,B}	29.3 ± 3.0^{B}	30.7 ± 2.1^{A,B}
1-year water storage	13.6 ± 1.3^{F}	18.3 ± 2.1^{E}	19.3 ± 1.5^{E}	20.1 ± 1.9^{E}	20.1 ± 1.3^{E}	24.0 ± 2.3^{D}
% reduction of bond strength	50	43	35	33	25	22

Superscript letters indicate significant differences (two-way ANOVA and Tukey's test, α = 0.05). *Prime & Bond Elect was used with Enforce. MBS: Monobond S; MB+: Monobond Plus.

Table 4 Mean bond strengths (MPa) of RelyX Ultimate to lithium disilicate

	No adhesive/ no silane	Adhesive*	Silane without MDP (MBS)	Silane without MDP (MBS) + adhesive*	Silane with MDP (MB+)	Silane with MDP (MB+) + adhesive*
Immediate	24.7 ± 1.5^{B}	27.4 ± 1.9^{A}	26.7 ± 2.7^{A}	23.9 ± 1.8^{B}	23.6 ± 2.5^{B}	24.9 ± 1.6^{A,B}
1-year water storage	12.5 ± 1.7^{E}	18.5 ± 1.9^{D}	19.5 ± 1.8^{D}	19.2 ± 1.5^{D}	19.9 ± 1.8^{D}	20.5 ± 2.5^{C}
% reduction of BS	50	32	27	20	16	18

Superscript letters indicate significant differences (two-way ANOVA and Tukey's test, α = 0.05). *Scotchbond Universal Adhesive was used with RelyX Ultimate. MBS: Monobond S; MB+: Monobond Plus.

Table 5 Mean bond strengths (MPa) to lithium disilicate: pairwise comparison*

	Immediate						1-year					
	No adhesive/ no silane	Adhesive**	Silane without MDP (MBS)***	Silane without MDP (MBS) + adhesive	Silane with MDP (MB+)	Silane with MDP (MB+) + adhesive	No adhesive/ no silane	Adhesive**	Silane without MDP (MBS)***	Silane without MDP (MBS) + adhesive***	Silane with MDP (MB+)	Silane with MDP (MB+) + adhesive
Enforce	27.1 ± 1.7	32.1 ± 1.7	29.9 ± 2.8	30.0 ± 0.9	29.3 ± 3.0	30.7 ± 2.1	13.6 ± 1.3	18.3 ± 2.1	19.3 ± 1.5	20.1 ± 1.9	20.1 ± 1.3	24.0 ± 2.3
Relyx Ultimate	24.7 ± 1.5	27.4 ± 1.9	26.7 ± 2.7	23.9 ± 1.8	23.6 ± 2.5	24.9 ± 1.6	12.5 ± 1.7	18.5 ± 1.9	19.5 ± 1.8	19.2 ± 1.5	19.9 ± 1.8	20.5 ± 2.5
Statistical analysis	Significant	Significant	Significant	Significant	Significant	Significant	Not significant	Not significant	Not significant	Not significant	Not significant	Significant

*T-test for independent samples (α = 0.05). Prime & Bond Elect** was used with Enforce and Scotchbond Universal Adhesive*** was used with RelyX Ultimate. MBS: Monobond S; MB+: Monobond Plus.

Chemical Interaction Analysis for Raman Spectroscopy

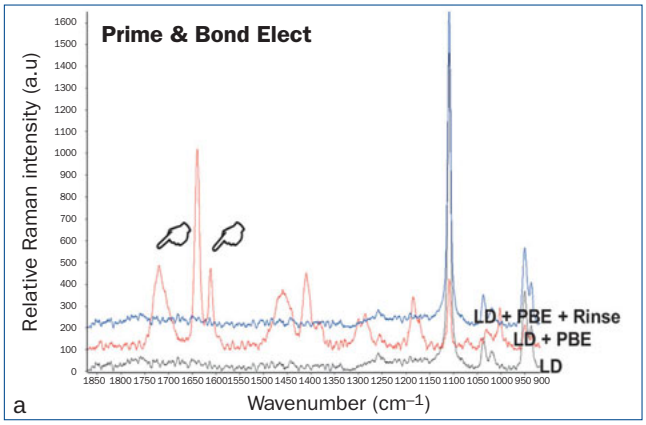
Representative micro-Raman spectra of the ceramics before and after application of adhesives associated or not with a separate silane solution are shown in Fig 1. The lithium disilicate ceramics (Li_2O-SiO_2) were characterized by a typical peak of Si-O (stretching vibration) in the region of 1100 cm^{-1}.[29] The adhesives were characterized by methacrylate peaks (1610 cm^{-1} [C=C aromatic], 1640 cm^{-1} [C=C aliphatic], and 1728 cm^{-1} [C=O carbonyl]). The adhesives were analyzed applied alone and combined with silane coupling agent. After rinsing, the methacrylate peaks were identified only for the SBU groups, regardless of the use of a separate silane coupling agent.

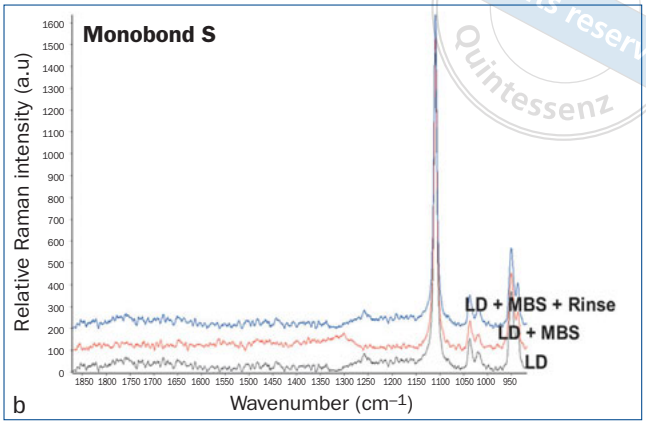
DISCUSSION

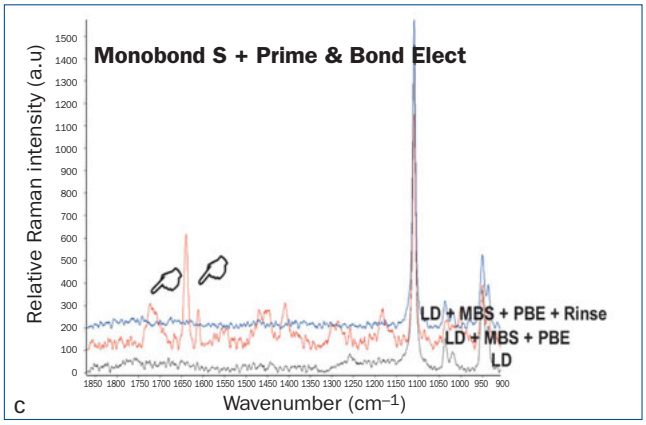
The present study investigated the effect of silanes, as well as the presence of MDP functional monomer in the silane solution, on the bonding of luting composites to LD ceramics. The use of a silane solution that included an MDP functional monomer (MB+) did not increase the mean μSBS. Therefore, we failed to reject the first null hypothesis.

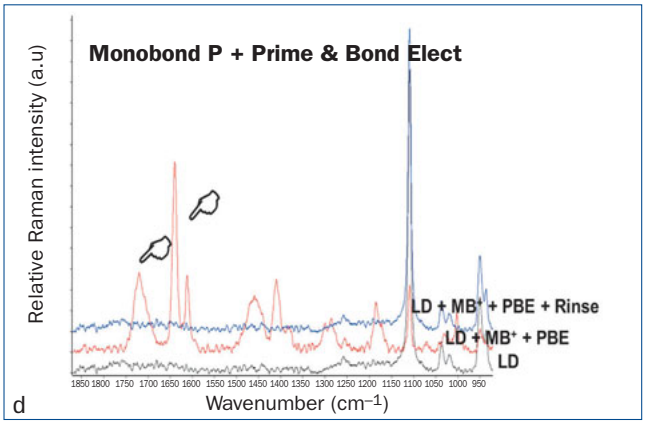
The silane coupling agent may play an important role in wettability in the absence of adhesive, since luting composites cannot penetrate into the irregular surfaces of the ceramics to create a stronger bond due to their relatively high viscosity.[14] The ceramic's hydrophilic surface becomes hydrophobic after silanization, allowing the luting material to optimally wet the LD surface.[10,36] This might explain why the silane solution alone increased the mean μSBS for both luting composites in the absence of an adhesive. However, the Raman analyses did not detect the characteristic silane groups (region of 1700 to 1728 cm^{-1}). Nevertheless, evidence was found of a silane-group (MBS) reaction, reflected in the weak decrease of Si-O (1100 cm^{-1}) compared to untreated LD (Fig 1B). This decrease of Si-O may be a result of the lower silane concentration present in the silane bottle. Usually, silane coupling agents can interact with sur-

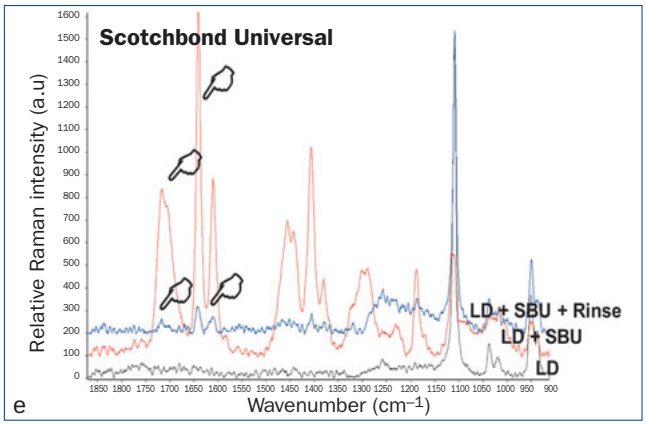
Fig 1 Representative Raman spectra for lithium disilicate (LD), adhesives (PBE and SBU), and silane coupling agents (MBS and MB+) combined with the adhesives and after rinsing, suggesting the chemical interaction/adsorption capacity. For all groups, the first spectrum (black) is representative only the ceramic surface, in which it is possible to identify the Si-O groups (strong peaks at 1100 cm^{-1}). The second spectrum (red) is representative of treatment under the ceramic surface (adhesive/silane coupling agent and adhesive); methacrylate peaks are evident (1610 cm^{-1} C=C aromatic, 1640 cm^{-1} C=C aliphatic, 1728 cm^{-1} C=O carbonyl) (black pointers on the top). The third spectrum (blue) is the result after rinsing. When just the silane agents were applied (B and F), the characteristic peaks did not appear; Si-O peaks decreased slightly (1100 cm^{-1}). Note that when both adhesives were applied on the ceramic surface, it was possible to identify all the methacrylate peaks, regardless of silane coupling agent use (red spectra). However, after rinsing, only the SBU groups, associated or not with silane, remained identifiable (black pointers on the top).

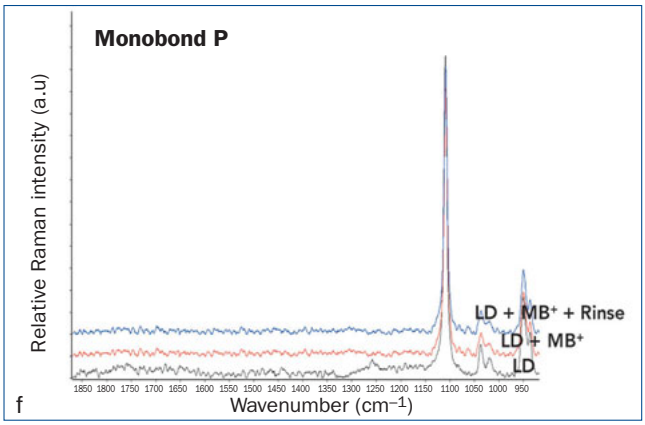


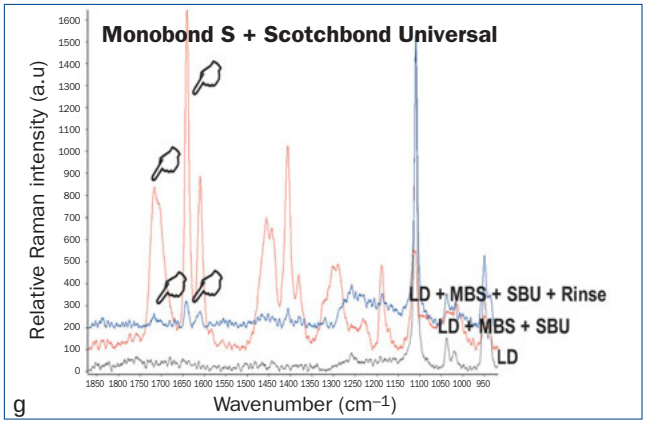


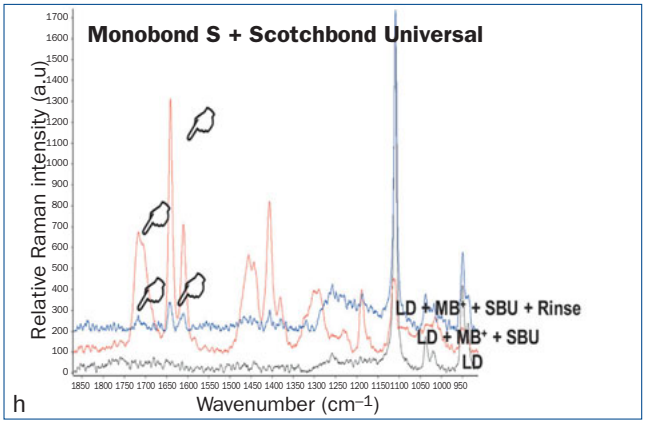












face silanols of the mineral (vertical condensation) by hydrolysis-condensation reactions, and react with themselves to form siloxanes by horizontal condensation. This reaction is mediated by hydrogen bonding to establish covalent bonds with silica, resulting in polymeric siloxane structures. However, the type of solvent, concentration of silane agent, amount of water, pH, temperature, etc, are important factors that define the interface formed between the silane and the surface of the crystalline phase of glass ceramics.[3,11] Therefore, the chemically bonded silane layer may have been unable to completely coat the LD surface.[3,11,34] This was also observed in the MB+ group spectrum (Fig 1F).

The role of the MDP functional monomer included in MB+ on the immediate bonding efficacy to LD remains unclear. During the silanization process, a condensation reaction occurs between the silanol groups of the silane agent and the crystalline phase of glass ceramics. The residual water is able to hydrolyze the silane. After this surface hydrolyzation, Si-OH-groups become accessible for chemical bonding. The water molecules can form hydrogen bonds to OH groups available on the filler surface.[13] This would explain why the Si-O peak (1100 cm^{-1}) increased slightly after rinsing and drying (Fig 1). It remains unclear, however, whether the MDP functional monomer would still be available to interact with the surface of the crystalline phase of the glass ceramics to induce stable bonds. The MDP interaction depends of several factors, such as concentration, structure of combined functional monomers, and solvent polarity, which consequently increases the complexity of the self-assembly environment.[59]

The results of the present study indicated that after 1 year of water storage, less reduction of mean bond strengths was observed for the groups in which an MDP-containing silane (MB+) was used for the two combinations of adhesive/luting composite. The presence of MDP may have helped maintain the stability of bonds to LD, as recently observed by Passia et al.[43] Those authors observed that the group in which an MDP solution containing silane was applied showed the lowest reduction of bond strengths when compared with groups without an MDP silane after 150 days of water storage associated with 37,500 thermocycles.

Subsequently, the present study analyzed the adhesive properties of the universal adhesive containg silane, in comparison with the use of silane or universal adhesive separately. The combination of a silane and universal adhesive in the same solution did not result in improved adhesive properties compared to the separate use of silane and universal adhesive for either luting composite, leading to rejection of the third null hypothesis.

Few studies have examined the role of universal adhesives as a one-step bonding procedure for glass ceramics, as the silane is often used as a separate step prior to the adhesive.[23,43] Our results are not in agreement with those of Passia et al.[43] The latter authors reported that the application of a silane containing MDP (MB+) showed higher immediate bond strengths than those of a universal adhesive. However, there was a possible confounding variable in that study, as silane and universal adhesive were combined with different luting composites, which may have influenced the results. Moreover, a different bond strength test was used in the present study than in that by Passia et al.[43]

HF etching followed by a silane solution is sufficient to improve bonding to LD when a universal adhesive containing silane is used, as observed in the present study. However, mean μSBS depends on other factors, including variation in chemical composition, wetting ability, viscosity, and mechanical properties of the luting composite, as previously mentioned by Lise et al,[30] which may explain the differences in 24-h mean μSBS for the two luting composites used in our study. The characteristics of the luting composite certainly play an important role.

Enforce, for example, showed significantly lower mechanical properties than a luting cement considered the predecessor of RelyX Ultimate (RelyX ARC),[16,18] which may explain why Enforce resulted in the lowest immediate and 1-year mean μSBS without adhesive or silane application. Resin-based materials with lower mechanical properties have been associated with lower bond strengths.[2,50]

Both universal adhesives applied without a separate silane step provided similar mean bond strengths compared to the multistep bonding protocol (we failed to reject the second null hypothesis). Apparently, the universal adhesive solution by itself promoted bonding to LD without the extra silane step. These findings are pertinent mainly if the different compositions of the two adhesives evaluated here are taken into consideration. While PBE is an MDP- and silane-free adhesive, SBU is a MDP- and silane-containing adhesive. The manufacturer of SBU claims that both components may facilitate bonding to indirect substrates.[1] In fact, the Raman analysis confirmed these claims, as only SBU remained attached to the LD surface after rinsing. According to the respective manufacturer, the SBU composition is a balanced mixture with methacrylate monomers, MDP functional monomer and silane, without the need for a separate ceramic primer step. Thus, it is reasonable to assume that the universal adhesive SBU is capable of interacting with the LD surface. In spite of this potential for chemical interaction, the results after 1-year water storage showed a significant reduction of mean bond strengths not only when SBU was applied without a separate silane step, but also when only PBE adhesive was applied. It also worth mentioning that the 1-year mean μSBS for both luting composites when only the respective adhesive was used were statistically similar to the respective mean μSBS when each of the silane solutions (MB+ and MBS) was used without any adhesive.

In terms of simplification, the use of a universal adhesive that can be applied on the tooth and the LD intaglio surface is very convenient. However, the combination of silane and resin monomers in universal adhesives has been controversial.[23,64] A recent paper[64] showed that a adhesive containing silane was not very effective or stable when applied under silica-glass plates (meant to represent silica-rich ceramics), most likely because the acidic solution promoted dehydration condensation.

The present study found that a significant reduction in mean bond strengths occurred for all groups after 1 year of water storage, which is in agreement with other authors.[19,21,23,27,32,43,62] This reduction leads to rejection of the fourth null hypothesis. This outcome may have a significant clinical impact, because LD restorations might fail clinically in the long term, as shown in systematic reviews of clinical studies of LD restorations.[24,48] However, only the combination of a silane containing MDP with either adhesive showed significantly higher mean bond strengths after 1 year of water storage when compared to other groups.

It has been reported that when a silanazed interface is exposed to water, a significant decrease of bond strength at the interface occurs over a long period of time, which may be due to the hydrolytic cleavage of siloxane bonds in the siloxane interfacial layer.[35,42] On the other hand, there is significant water sorption when adhesives are exposed to water.[33,51] This leads to plasticized polymers and lowers their mechanical properties,[15,51] resulting in lower bond durability.[12] Although the bonding interface on LD is more hydrophobic than a bonding interface on dentin, the contact of the interface with water causes the same degradation, as previously observed,[19,21,23,27,32,43,62] but to a lesser extent.

However, the association of MB+ with adhesives yielded better results in terms of bond strength after 1-year water storage. A more plausible explanation for these results is the fact that the adhesive coating may protect the surface of the MDP-containing silane. This protective effect on the silane layer, maintaining the bonding of silane to LD, may partly preserve the bond strength after 1-year water storage. Of course, the degradation process of adhesive with or without separate silane application is the same, and this is probably responsible for lower bond strength of the LD interface after 1-year water storage. Unfortunately, this protective effect did not occur when a silane without MDP (MBS) was used. This is probably related to the fact that MDP in MB+ helps maintain the bond strength after water storage.

The silane solution becomes unstable when combined with MDP and bis-GMA.[10,31] In the acidic environment produced by MDP, a self-condensation reaction may occur in the silane.[31,64] When the silane is separate from the methacrylate-based adhesive, such as in a silane-MDP solution, MDP enhances the hydrolytic stability of the solution, as shown for MDP-based luting agents. In fact, MDP forms more stable monomer-Ca salts (nanolayering) than other carbon-chain monomers, which is the reason why adhesives containing MDP result in more durable bonding,[66] as previously shown when bonding to dentin.[39]

It worth mentioning that the microshear bond strength method was used in the present study because it results in a lower coefficient of variation when compared to other dentin bond strength testing methods.[52] In dentin, the coefficient of variation is close to 20%, but on the surface of ceramic, the values are as low as 5% to 10%, as confirmed in the current and a previous study.[32]

CONCLUSION

The present results do not support the use of a simplified bonding protocol that includes either a silane or a universal adhesive. More stable bonding after water storage was obtained when a silane containing MDP was associated with a universal adhesive.

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Clinical relevance: The use of a separate MDP-based silane coupling agent may result in better clinical performance of universal adhesives for luting lithium disilicate restorations.