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Effect of Methacryloyloxydecyl Dihydrogen Phosphate–Containing Silane and Adhesive Used Alone or in Combination on the Bond Strength and Chemical Interaction With Zirconia Ceramics Under Thermal Aging

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Clinical Relevance

Achieving durable bonding to zirconia is fundamental for the application of a methacryloyloxydecyl dihydrogen phosphate (MDP)–containing silane solution or an MDP-containing silane solution associated with an MDP-containing universal adhesive.

SUMMARY

Objectives: To evaluate the effect of a methacryloyloxydecyl dihydrogen phosphate (MDP)–containing silane coupling agent and universal adhesive, used alone or in combination, on the microshear bond strength (μSBS) to zirconia after 24 hours of water storage (24h) and after 10,000 thermocycles (TC), complemented with

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chemical analysis of the surface to establish the presence of MDP on the surface of the zirconia after bonding procedures.

Methods and Materials: Thirty computer-aided design/computed-aided manufacturing blocks of zirconia were cut into four sections (6×6×6 mm) and sintered. Zirconia sections (n=96) were assigned to 24 groups according to three factors: 1) silane (no silane, Monobond S [MBS], Monobond P [MB$^+$]), 2) adhesive + resin cement (no adhesive + Enforce [ENF], no adhesive + RelyX Ultimate [REX], Prime&Bond Elect + Enforce [PBE/ENF], Scotchbond Universal + RelyX Ultimate [SBU/REX]), and 3) thermocycling (no thermocycling [24h], 10,000 thermocycles [TC]). Upon silane/adhesive application, cylinder-shaped matrices were filled with resin cement and light cured. Specimens were tested in μSBS (1.0 mm/min) after 24h or TC. The μSBS data were analyzed using two-way ANOVA and Tukey's post hoc test (α=0.05). In addition, micro-Raman spectroscopy was used to analyze the zirconia surface for immediate chemical interaction analysis (n=24).

Results: For the 24h condition, PBE/ENF resulted in lower mean μSBS than both groups with silane without PBE (MBS and MB$^+$ groups; $p<0.001$). SBU alone or MB$^+$ alone and MB$^+$ associated with SBU showed the highest mean μSBS ($p<0.001$). For the TC condition, all groups showed a significant decrease in mean μSBS compared with those of 24h ($p<0.001$), with the exception of MB$^+$ associated to SBU ($p>0.05$). However, the application of MB$^+$ alone or MB$^+$ associated to SBU resulted in higher mean μSBS ($p<0.001$) after TC than the remaining TC groups. In terms of chemical interaction, only the SBU groups, alone or combined with both of the silane agents, were associated with the methacrylate groups after rinsing.

Conclusions: The results of the current study support the use of an MDP-containing silane solution or an MDP-containing silane solution associated with an MDP-containing universal adhesive for bonding to air-abraded zirconia, as a more stable bonding after thermocycling.

INTRODUCTION

Zirconia-based ceramics (zirconia) have been used as biomaterials for orthopedic and dental prostheses, holding a unique place among oxide ceramics because of their excellent biomechanical properties, such as flexural strength, resistance to crack propagation, biocompatibility, adequate esthetics, and stability.[1-4] These superior mechanical properties compared with those of other all-ceramic materials make zirconia an excellent material for crowns, bridges, and frameworks in the anterior and posterior region.[5,6] Most of the zirconia that is currently used in dentistry is tetragonal zirconia polycrystals stabilized with 3 mol% of yttria (3Y-TZP).[1,4]

One of the major limitations of the use of zirconia is the difficulty of adhering to this material.[7] Different luting cements have been suggested for zirconia restorations, including glass-ionomer cements, conventional resin cements, and self-adhesive resin cements. Nevertheless, resin cements are generally preferred for cementation of zirconia to improve retention and to obtain sealed restorations.[8] Resin bonding to glass-matrix ceramics is achieved by etching the surface with hydrofluoric acid to partially dissolve the glass phase and create porosities for micromechanical attachment. A silane coupling agent is then applied to provide chemical adhesion to silica.[9,10] As zirconia does not contain a glass phase, hydrofluoric acid etching is less effective on zirconia than on glass-matrix ceramics, when applied under the same conditions.[2,11] The lack of silica in zirconia may also preclude chemical bonding with silane, making conventional silane less effective for zirconia bonding.[2,12,13] Consequently, creating predictable and durable bonding to zirconia is challenging, and the most effective clinical protocol is still under discussion.[14-17]

Although no correlation has been found between surface roughness and tensile bond strength, indicating the importance of chemical bonding to zirconia,[18] air-abrasion methods have been used to increase the surface area for micro-mechanical interlocking, including alumina air abrasion and tribochemical silica coating.[19-23] In addition, specific primers have been recently introduced to enhance chemical bonding to zirconia. The latest examples are phosphate monomer–based primers (eg, Monobond Plus, Ivoclar Vivadent, Schaan, Liechtenstein), which promote chemical adhesion between resin materials and the hydroxyl groups present on the zirconia surface.[12,14,24,25]

Monobond Plus contains methacryloyloxydecyl dihydrogen phosphate (MDP) in an alcohol solution of a silane (3-methacryloxypropyl-trimethoxysilane, and sulfide methacrylate). The idea behind this universal primer is to make the clinical bonding

procedure easier than having to apply a separate silane and a separate adhesive. However, despite promising results, only a few studies have focused on the efficacy of this specific primer to bond to zirconia.[25-29]

Concomitantly with the introduction of adhesion-promoting primers for zirconia, a novel family of adhesive systems, known as "universal" adhesives, has been developed.[30-33] Most universal adhesives contain functional monomers, such as MDP. For enamel and dentin, universal adhesives are recommended as etch-and-rinse (two-step) or self-etch (one-step) adhesives. More recently, the indication for universal adhesives has been extended to other substrates, including resin composite, glass-matrix ceramics, oxide-based ceramics, and metal alloys, without the need for additional primers.[21,34,35]

Several studies have reported that the application of universal adhesives provides higher bond strengths to zirconia than the application of zirconia primers.[14,23,34,36] Nevertheless, two studies[37,38] found no differences between a zirconia primer and a universal adhesive. Therefore, there is still controversy in the literature as to whether universal adhesives can replace zirconia primers.

Thus, the aim of this study was to evaluate the effect of silane with or without MDP and the effect of universal adhesives with or without MDP on the bonding ability of resin cements to zirconia, after 24 hours of water storage and after 10,000 thermocycles (TC), using microshear bond strength (μSBS) testing. In addition, chemical analysis of the surface by micro-Raman spectroscopy was performed to establish the presence of MDP on the surface of the zirconia after bonding procedures as a complementary evaluation. The null hypotheses tested were 1) the use of a silane and universal adhesive combined will not influence the long-term bonding to zirconia when compared with the use of separate silane and separate universal adhesive, 2) an MDP-containing silane will not influence the long-term bonding to zirconia when compared with a silane without MDP, and 3) a universal adhesive containing MDP will not influence the long-term bonding to zirconia when compared with an MDP-free universal adhesive.

METHODS AND MATERIALS

Specimen Preparation

A total of 30 computer-aided design/computed-aided manufacturing blocks (12×12×6 mm) of yttria-tetragonal zirconia polycrystal (zirconia; Ceramill, Amann Girrbach AG, Koblach, Austria) were used. All blocks were cut into four rectangular sections (6×6×6 mm) (n=120) using a diamond disc on slow speed (Isomet, Buehler, LakeBluff, IL, USA) under water cooling. After ultrasonically cleaning in distilled water for 15 minutes, the zirconia sections were sintered in a furnace (Ceramill Therm, Amann Girrbach AG) using a universal program of 8°C per minute from 200°C to 1450°C, after two hours at a fixed temperature of 1450°C, and the correct cooling time.

Experimental Design

Ninety-six zirconia sections were randomly assigned (http://www.sealedenvelope.com) into 24 experimental conditions to evaluate the μSBS (n=4) according to the following independent variables: 1) silane (no silane, Monobond S [MDP-free silane; MBS], Monobond Plus [MDP-containing silane; MB^+), 2) universal adhesive + resin cement (no adhesive + Enforce [ENF], no adhesive + RelyX Ultimate [REX], Prime&Bond Elect [silane-free and MDP-free universal adhesive] + Enforce [PBE/ENF], Scotchbond Universal Adhesive [silane- and MDP-containing universal adhesive] + RelyX Ultimate [SBU/REX]), and 3) thermocycling (no thermocycling [24h] or after 10,000 TC). To evaluate the chemical interaction of silane and universal adhesives with zirconia surfaces by micro-Raman spectroscopy in the immediate time period, 24 zirconia sections were randomly assigned (http://www.sealedenvelope.com) into eight experimental conditions (n=3) (silane vs universal adhesive + resin cement). The composition, application mode, and batch numbers are described in Table 1.

Microshear Bond Strength (μSBS)

All zirconia sections were mounted in a polyvinyl chloride (PVC) ring filled with acrylic resin (Auto-Clear, DentBras, Pirassununga, São Paulo, Brazil) displaying the zirconia surface with a height of 3 mm on the top of the cylinder. The sections were sandblasted with <50 μm Al_2O_3 particles (2.8 bar, seven seconds), ultrasonically cleaned in distilled water for 180 seconds, washed in 96% ethanol, and dried with oil-free air. The silane and universal adhesives were then applied according to the respective manufacturer's instructions (Table 1). A single operator performed all bonding procedures.

Subsequently, seven polyethylene transparent Tygon tubes (Tygon Medical Tubing Formulations 54-HL, Saint Gobain Performance Plastics, Akron, OH, USA), with an internal diameter of 0.8 mm and

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, sulfide 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 Sirona (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 Oral Care (523652)	10-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 (ENF)	Dentsply Sirona (108813H)	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 (REX)	3M Oral Care (564178)	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, TEGDMA, 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.

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

a height of 0.5 mm, were positioned over the zirconia surface in each specimen. The resin cement (Table 1) was carefully packed inside each tube, and a clear Mylar matrix strip was placed over the filled Tygon tube and pressed gently into place. The resin cement was light cured for 20 seconds using a light-emitting diode light-curing unit set at 1200 mW/cm^2 (Radii-cal, SDI Limited, Bayswater, Victoria, Australia). A radiometer (Demetron L.E.D. Radiometer, Kerr Sybron Dental Specialties, Middleton, WI, USA) was used to check the light intensity every five specimens. These procedures were carried out under magnifying loupes.[39]

After bonding procedures, all zirconia sections were stored in distilled water for 24 hours at 37°C. After storage, the Tygon tubes from all zirconia sections were carefully removed with a blade to expose the cement cylinder specimen. Each specimen was examined under a stereomicroscope at 10× magnification. The cement specimen was discarded if there was evidence of porosity or gaps at the interface. Half of the groups were tested after 24 hours of storage in water, and the other half were tested after 10,000 TC between water baths held at 5°C and 55°C, with a dwell time of one minute.[22]

Each PVC ring with the zirconia section was attached to a shear-testing fixture (Odeme Biotech-

nology, Joaçaba, SC, Brazil) and tested in a universal testing machine (Kratos IKCL 3-USB, Kratos Equipamentos Industriais Ltda, Cotia, São Paulo, Brazil). Then, the set zirconia section fixture was placed in the universal testing machine, and a thin orthodontic wire (0.2-mm diameter) was looped around the base of each resin cement cylinder. The setup was kept aligned (resin cement-zirconia interface, the wire loop, and the center of the load cell) to ensure the correct orientation of the shear forces.[40] The cross-head speed was set at 1 mm/min until failure.

The μSBS (MPa) was 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 Ltd, Tokyo, Japan) at 100× magnification to define the location of the bond failure. The failure mode was classified as adhesive/mixed (failure at the resin cement–zirconia interface, which may include cohesive failure of the neighboring substrates), cohesive in resin cement (failure exclusively within resin cement), or cohesive in zirconia (failure exclusively within zirconia). Also, premature failures (PFs) before the test were recorded. A PF was considered as a specimen that showed porosities or other defects when examined under an optical microscope at 50× or a specimen that showed spontaneous fracture during testing.

Chemical Interaction Analysis for Micro-Raman Spectroscopy

Two zirconia sections for each experimental treatment group were analyzed immediately. A micro-Raman spectrometer (Horiba Scientific, Tokyo, Nagoya, Japan) was first calibrated for zero and then for coefficient values using a silicon specimen. Zirconia sections were analyzed using the following Raman parameters: 20 mW HeNe laser with 632.8 nm wavelength (green laser at 532 nm), with a spectral resolution at 1 cm^{-1}, accumulation time of 30 seconds, with two coadditions, and magnification of 20× (Olympus UK, London, UK) in a range of 100-1800 cm^{-1}. First, spectra were taken of silanes, uncured universal adhesives, and the zirconia surface separately. Then, each silane and each universal adhesive was applied according to the respective manufacturer's instructions (Table 1). The zirconia sections were subsequently rinsed for one minute in distilled water (30 seconds) and absolute ethanol (30 seconds), as described by Yoshihara and others,[41] to remove the components that remained on the zirconia surface without chemically interacting with the substrate. The spectra were obtained in triplicate, and a comparison was carried out by spectra subtraction and thus analyzed qualitatively.

Statistical Analysis

Before submitting the data for analysis using the appropriate statistical test, the Kolmogorov-Smirnov test was performed to assess whether the data followed a normal distribution, and the Bartlett's test for equality of variances was performed to determine if the assumption of equal variances was valid.[42] After observing the normality of the data distribution and the equality of the variances, the μSBS (MPa) data were subjected to a parametric statistical analysis. All premature failures were excluded from the statistical analysis. The μSBS data were analyzed using two-way analysis of variance (silane vs thermocycling) for each combination of adhesive + resin cement. Tukey's post hoc test was used at $\alpha = 0.05$.

RESULTS

Microshear Bond Strength (μSBS)

No specimens were discarded because of porosities or other defects. Most of the specimens showed adhesive/mixed failures (Table 2). However, there was an increased number of PFs for most of the groups after TC (Table 2).

Enforce resulted in the lowest 24h mean μSBS ($p<0.0001$; Table 3) when neither PBE adhesive nor silane was used. The use of PBE without any silane, or PBE associated with MBS, showed statistically similar and intermediary 24h mean μSBS ($p>0.05$; Table 3). The use of MBS alone or MB^+ associated with PBE resulted in significantly higher 24h mean μSBS compared with the use of the adhesive PBE without any silane ($p<0.0001$; Table 3). The application of MB^+ without any adhesive showed the highest 24h mean μSBS when compared with all other groups ($p<0.0001$; Table 3). After TC, all groups showed a significant decrease in mean μSBS ($p<0.0001$; Table 3). For five of the six groups, the percentage reduction in mean μSBS ranged from 73% to 91%. The only exception was the MB^+ silane group, which showed higher TC mean μSBS than the other five groups, with only a 32% reduction in mean μSBS ($p<0.001$; Table 3) compared with the respective 24h mean μSBS.

RelyX Ultimate resulted in the lowest 24h mean μSBS ($p<0.0001$; Table 3) when neither SBU adhesive nor silane was used. The use of MBS alone

Table 2: *Number (%) of Specimens According to Fracture Mode*

Resin Cement	Fracture Mode							
	24h				TC			
	A/M	CC	CZ	PF	A/M	CC	CZ	PF
Enforce[a]								
No adhesive/no silane	28 (100)	0 (0)	0 (0)	0 (0)	16 (52)	0 (0)	0 (0)	12 (48)
Adhesive	28 (100)	0 (0)	0 (0)	0 (0)	21 (72)	0 (0)	0 (0)	7 (28)
Silane without 10-MDP (MBS)	27 (96)	1 (4)	0 (0)	0 (0)	22 (76)	0 (0)	0 (0)	6 (24)
Silane without 10-MDP (MBS) + adhesive	28 (100)	0 (0)	0 (0)	0 (0)	18 (60)	0 (0)	0 (0)	10 (40)
Silane with 10-MDP (MB^+)	27 (96)	1 (4)	0 (0)	0 (0)	25 (88)	3 (12)	0 (0)	0 (0)
Silane with 10-MDP (MB^+) + adhesive	28 (100)	0 (0)	0 (0)	0 (0)	20 (68)	2 (8)	0 (0)	6 (24)
RelyX Ultimate[b]								
No adhesive/no silane	28 (100)	0 (0)	0 (0)	0 (0)	19 (64)	0 (0)	0 (0)	9 (36)
Adhesive	28 (100)	0 (0)	0 (0)	0 (0)	22 (76)	0 (0)	0 (0)	6 (24)
Silane without 10-MDP (MBS)	27 (96)	1 (4)	0 (0)	0 (0)	24 (84)	0 (0)	0 (0)	4 (16)
Silane without 10-MDP (MBS) + adhesive	27 (96)	1 (4)	0 (0)	0 (0)	27 (96)	0 (0)	0 (0)	1 (4)
Silane with 10-MDP (MB^+)	27 (96)	1 (4)	0 (0)	0 (0)	24 (84)	2 (8)	0 (0)	2 (8)
Silane with 10-MDP (MB^+) + adhesive	28 (100)	0 (0)	0 (0)	0 (0)	24 (84)	3 (12)	0 (0)	1 (4)

Abbreviations: A/M, adhesive/mixed (failure at the cement-zirconia interface, which may include cohesive failure of the neighboring substrates); CC, cohesive in cement (failure exclusively within cement); CZ, cohesive zirconia (failure exclusively within zirconia); 24h, 24 hours of water storage; TC, after thermocycling; MB^+, Monobond Plus (Ivoclar Vivadent); MBS, Monobond S (Ivoclar Vivadent); 10-MDP, 10–methacryloyloxydecyl dihydrogen phosphate; PF, premature failures (failure before the test).
[a] Prime&Bond Elect was used with Enforce (Dentsply Sirona).
[b] Scotchbond Universal Adhesive was used with RelyX Ultimate (3M Oral Care).

or MBS associated with SBU showed significantly higher 24h mean μSBS only when compared with groups with no silane/no adhesive ($p<0.0001$; Table 3). RelyX Ultimate resulted in a significantly higher 24h mean μSBS ($p<0.001$; Table 3) when the SBU adhesive or MB^+ was used alone, as well as when MB^+ was associated with SBU. After TC, most groups showed a significant decrease in mean μSBS ($p<0.0001$; Table 3). However, the application of resin cement with no silane/no adhesive or associated to SBU, as well as the application of MBS alone, resulted in the lowest mean μSBS after TC, while the application of MB^+ alone or associated with SBU showed a similar higher mean μSBS after TC than the other four groups ($p>0.05$; Table 3).

Chemical Interaction Analysis for Micro-Raman Spectroscopy

Representative Raman spectra obtained with zirconia treated according to the experimental conditions, as well as after rinsing, are shown in Figure 1. The zirconia specimens were identified by the characteristic peaks of the ZrO_2 groups (267 cm^{-1}, 335 cm^{-1}, 476 cm^{-1}, 637 cm^{-1}),[43,44] which were identified in all

Table 3: *Mean of Bond Strengths (MPa) for Enforce and RelyX Ultimate to Zirconia[a]*

	No Adhesive/ No Silane	Adhesive[b]	Silane Without MDP (MBS)	Silane Without MDP (MBS) + Adhesive	Silane With MDP (MB^+)	Silane With MDP (MB^+) + Adhesive
24h Enforce	5.6 ± 1.3 dA	22.9 ± 2.1 cA	29.9 ± 2.8 bA	27.9 ± 7.2 bcA	36.3 ± 3.3 aA	30.4 ± 0.3 bA
TC Enforce	1.5 ± 0.1 cB	3.5 ± 0.3 bcB	5.9 ± 2.7 bB	2.6 ± 0.8 bcB	24.6 ± 3.2 aB	5.5 ± 3.0 bB
% reduction of BS	73	85	80	91	32	82
24h RelyX Ultimate	17.2 ± 1.9 eA	29.0 ± 1.1 bA	26.7 ± 2.7 cA	21.2 ± 4.8 dA	31.5 ± 4.3 abA	27.5 ± 1.6 bcA
TC RelyX Ultimate	7.7 ± 2.3 cB	11.6 ± 1.3 cB	10.4 ± 1.6 cB	15.1 ± 2.9 bB	26.5 ± 1.7 aB	26.2 ± 5.3 aA
% reduction of BS	55	60	61	28	16	5

Abbreviations: 24h, 24 hours of water storage; BS, bond strength; MB^+, Monobond Plus (Ivoclar Vivadent); MBS, Monobond S (Ivoclar Vivadent); MDP, methacryloyloxydecyl dihydrogen phosphate; TC, after thermocycling.
[a] Comparisons are valid only within resin cement. Different lowercase letters represent statistically significant differences within the same line ($p<0.05$; horizontal comparisons). Different uppercase letters represent statistically significant differences within the same column ($p<0.05$; vertical comparisons). Two-way analysis of variance and Tukey's test ($\alpha=0.05$).
[b] Prime&Bond Elect was used for Enforce (Dentsply Sirona), and Scotchbond Universal was used for RelyX Ultimate (3M Oral Care).

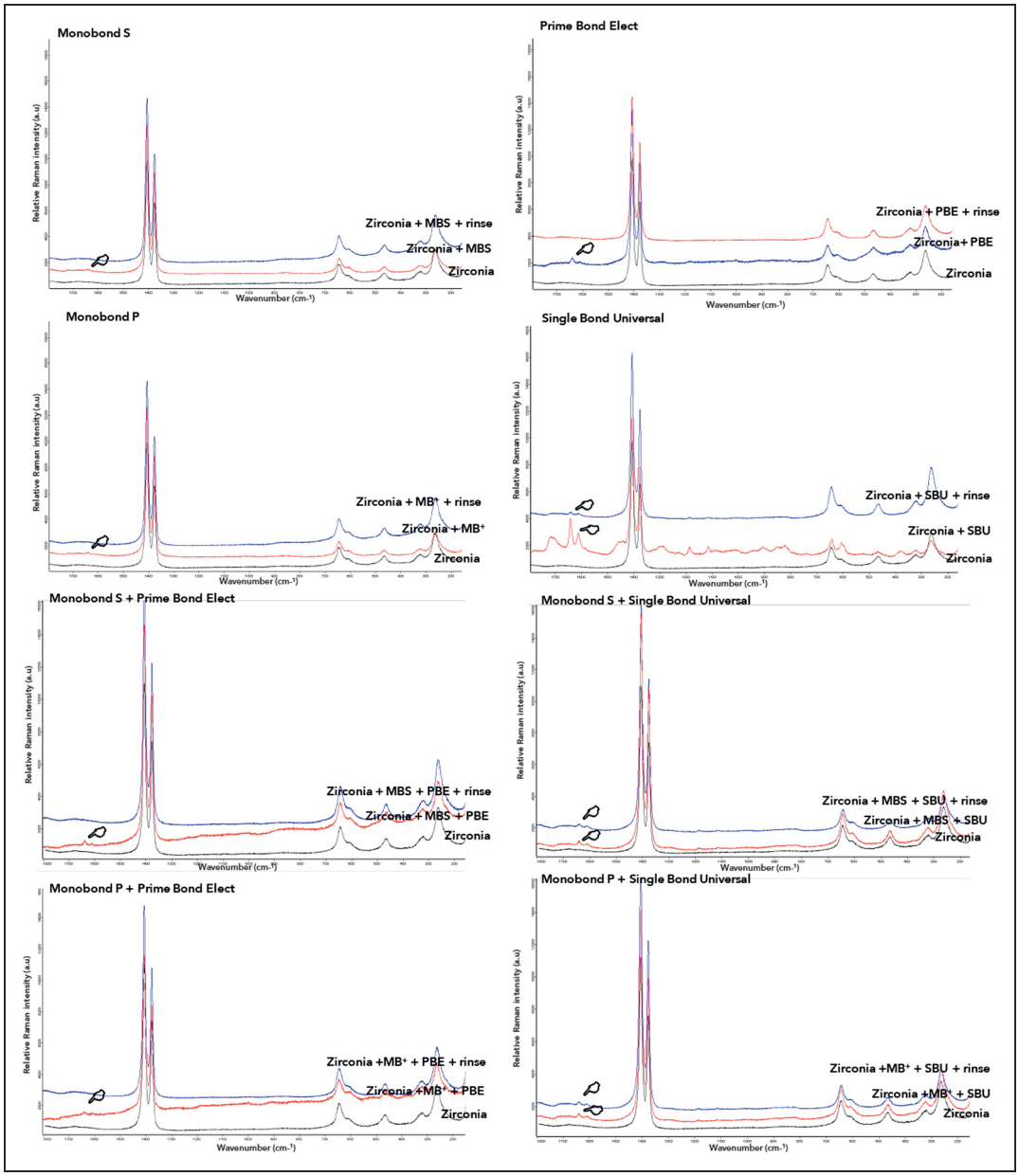

Figure 1. *Representative Raman spectra for zirconia, adhesives (PBE and SBU), and silane coupling agents (MBS and MB^+) combined with the adhesives and after rinsing, suggesting the chemical interaction/adsorption capacity. For all groups, the first spectrum (black) is representative only of the zirconia surface, in which it is possible to identify the ZrO_2 groups (267 cm^{-1}, 335 cm^{-1}, 476 cm^{-1}, 637 cm^{-1}, 1380 cm^{-1}, and 1420 cm^{-1} peaks). The second spectrum (red) is representative of treatment of 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. In this case, only the SBU groups (alone or combined with both the silane agents) are associated with the methacrylate groups (black pointer), suggesting that the monomer is kept on the zirconia surface, regardless of the presence of MDP in the silane agent.*

spectra. The methacrylate peaks in the adhesives or silanes, as well as the combination of them, were characterized (1610 cm^{-1} [C=C aromatic], 1640 cm^{-1} [C=C aliphatic]) and identified in all spectra after treatment. However, in terms of chemical interaction, only the SBU groups, alone or combined with both of the silane agents, were associated with the methacrylate groups after rinsing, suggesting that the monomer is kept on the zirconia surface, regardless of the presence of MDP in the silane agent.

DISCUSSION

Strong and durable adhesion to dental zirconia has eluded researchers for more than 10 years. System-

atic reviews have reported that, while mechanical and chemical pretreatment improve *in vitro* bonding to zirconia, adhesive monomers may be needed for durable chemical bonding.[15-17] Nevertheless, MDP-based resin cements may result in improved bonding effectiveness compared to other cement types.[17]

While Nagaoka and others[45] reported increasing bond strengths to zirconia for higher concentrations of MDP up to 1 wt%, a recent article compared experimental primers with different concentrations of MDP (3% to 15%) with a primer without MDP. The immediate bond strengths to polished zirconia showed that the presence of MDP was more important for bonding to zirconia than the concentrations evaluated.[46]

Also, Yoshida and others[12] reported that 10,000 TC significantly reduced the bond strengths for concentrations of MDP up to 1 wt%. These results after TC cannot be directly compared with our results, as the concentration of MDP in current commercial MDP-containing zirconia primers is higher than 1 wt%.[45] More recently, Go and others[47] confirmed that an increased MDP concentration did not lead to an additional enhancement in bond strength. These authors showed that the presence of MDP in a luting cement or in a primer was more important for bond strength to zirconia than the application of MDP-containing primer association with MDP-based resin cements. Another study used air-abraded zirconia[24] and reported that two MDP-containing primers were able to maintain bonding durability after water storage with TC as compared with when an MDP-free primer or no primer was used.

MB^+ associated with SBU was the only group in our study for which there was not a significant reduction in mean bond strengths after TC; therefore, the first null hypothesis was rejected. Coincidentally, this was the only group for which MDP was present both in the silane and in the adhesive. MDP, either included in the composition of primers or luting cements, provides chemical bonding between methacrylate-based materials and the zirconium oxide layer present on the surface of 3Y-TZP (zirconia).[12,45,48] While a study using secondary ion mass spectrometry suggested a chemical bond between zirconia and an MDP-containing primer,[49] the X-ray photoelectron spectroscopy results obtained by Xie and others[37] provided irrefutable evidence of chemical bonding, revealing that ZrO_2-MDP was well formed, with a high ratio of ZrO. More recently, Nagaoka and others[45] reported a novel chemical-bonding mechanism involving hydrogen-bonding interactions between neighboring adsorbed phosphate groups from the MDP molecule, which might simultaneously interact with zirconia via ionic bonding.

According to Yoshida and others,[12] MDP may also react with zirconia through hydroxyl groups present on both the MDP molecule and the zirconia surface. This was also discussed by Piascik and others,[50] who reported that when the zirconia surface reacts with a phosphate ester–containing monomer (such as MDP) in the adhesive, hydroxyl groups on the ester can form hydrogen bonds with surface hydroxyl groups.[49]

The pH of the solution has been reported to influence the structure of silanes.[12,51] When MB^+ is applied to surfaces with hydroxyl groups, the silane component is hydrolyzed in the presence of the acidic monomer MDP.[12] While silane bonds to hydroxyl groups on glass-matrix ceramic surfaces, these same hydroxyl groups are sparsely distributed on the zirconium oxide layer,[18] occupying 5.4% of the entire surface. This might be enough to guarantee high 24h mean μSBS to zirconia, as MB^+ resulted in the highest 24h mean μSBS for both resin cements (Table 3).

However, the application of a second coating of silane, included in the composition of SBU adhesive, might be able to react with the residual hydroxyl groups provided by the silane from the previously applied MB^+, providing some kind of shielding effect to the MDP-containing silane. In addition, the methacrylate groups in SBU, including MDP, may copolymerize with the methacrylate groups of both silanes (including the methacrylate radical in 3-methacryloyloxypropyl trimethoxysilane of MBS and MB^+), a reaction previously described[21] for the interaction between this same silane molecule and a conventional resin cement. Nonetheless, this mechanism would not be solely responsible for this chemical reaction, as PBE, an MDP-free adhesive, resulted in a significant decrease (82%) in mean μSBS after TC when it was applied over MB^+ (Table 3). Actually, PBE may be too hydrophilic, as it does not contain 10-MDP. This monomer is quite hydrophobic because of its long carbonyl chain.[52] The hydrophilicity of PBE might be responsible for water degradation of the adhesive interface after TC.

On the other hand, the interaction between the MB^+ molecule and SBU may be significantly improved with the chemical bonding provided by the MDP molecule, making these reactions responsible for the statistically similar mean μSBS of MB^+

associated to SBU before and after TC or for the smaller reduction in mean μSBS when MDP was not included in the silane (MBS associated to SBU). In fact, our Raman results suggest the chemical interaction of SBU with the zirconia surface independent of the application of a silane. The inclusion of MDP in the composition of SBU might explain the identification of a Raman peak after rinsing, which is compatible with a monomer. Future studies will need to be carried out to evaluate whether this interaction occurs when different MDP-containing universal adhesives are applied to the zirconia surface.

Notwithstanding, some authors have suggested that the acidity (pH=3.1) of MB^+ is responsible for the decrease in bond strengths to zirconia[53] and subsequent hydrolysis of the silane component in acidic solution. It seems that the application of a less acidic MDP-containing silane did not jeopardize the bond strength to zirconia.[47] In fact, MDP bonds more efficiently to zirconia in alkaline conditions.[54]

However, the formation of polysiloxane structures after the application of the silane-containing adhesive (SBU) on the zirconia surface previously treated with MB^+ may be another potential mechanism to explain the stronger bonds of MB^+ associated with SBU after TC compared with the application of MB^+ or SBU separately. In fact, when MB^+ was applied without adhesive followed by RelyX Ultimate or Enforce (Table 3), the mean μSBSs were statistically lower after TC, corresponding to a decrease of 16% and 32%, respectively. When SBU or PBE was applied without any silane, the reduction in mean μSBS after TC was extremely abrupt (60% and 85%, respectively; Table 3), which was identical to the reduction observed with the application of an MDP-free silane (MBS) without adhesive (61% and 80%, respectively, for RelyX Ultimate or Enforce; Table 3). Therefore, the second hypothesis was rejected.

This difference may suggest that an MDP-containing silane solution, MB^+, is more crucial to adhesion to zirconia than the MDP-containing adhesive, SBU. The combination of an MDP-free silane (MBS) with SBU still resulted in a statistically lower mean μSBS after TC, although the reduction was not as pronounced as that observed for the groups in which silane and adhesive were applied separately (28% for the former when compared with 60%-61% for the silane and adhesive alone). Likewise, when Enforce was used, the application of MB^+ alone resulted in the lowest reduction in mean μSBS after TC (32%) in comparison with all the remaining Enforce groups, which displayed a 73% higher reduction in mean μSBS.

Interestingly, the application of MB^+ associated with PBE resulted in a significant decrease in mean μSBS after TC (82%) when compared with MB^+ alone (32%). The application of PBE, an MDP-free adhesive, might have protected the silane layer, especially when the MDP-containing silane (MB^+) was used. However, the application of PBE deteriorated the 24h mean μSBS to zirconia, with greater deterioration, after TC. This result indicates the rejection of the third hypothesis.

PBE is an acetone-based adhesive, while SBU is an ethanol-based adhesive. As acetone evaporates faster than ethanol,[52] the application of only one coat of PBE may have been insufficient to promote a complete protection on the silane layer as previously reported for bonding to dentin.[55,56] Also, PBE is more acidic than SBU. While the pH of PBE is 2.5, SBU has a pH range of 2.7 to 3.0.[31,56,57] The higher acidity of PBE could decrease the pH of the silane solution and boost the decrease in bond strength to zirconia, as previously shown.[54] Future studies need to be carried out to evaluate the effect of universal adhesives with different pH on the interaction with zirconia.

In fact, this reduction of bond strength also occurred when the MDP-free silane MBS was used. An extreme reduction of 91% in mean μSBS after TC occurred for the combination of MDP-free silane and PBE, as well as for the MDP-containing silane associated to PBE (82%; Table 3), suggesting that the use of PBE itself may not boost chemical bonding to zirconia intermediated by a silane. Actually, the absence of MDP, presence of acetone, and lower pH also help to explain the lower mean μSBS after TC for PBE, as well as the higher percentage of premature failures when compared with SBU. Although there was a very similar fracture pattern between different groups at 24h and after TC, PBE had a 27.3% rate of PFs compared with 15.3% for SBU.

It is worth mentioning that, in all groups of the present study, the adhesive + resin cement from the same manufacturer were compared. This approach was followed because, during a luting procedure, the clinician usually applies adhesive + resin cement from the same manufacturer. A closer view of the results shows that in several groups, the luting procedure realized with Enforce resulted in lower 24h and TC mean μSBS than RelyX Ultimate, mainly after TC. This means not only that the

silane/adhesive materials could be responsible for the degradation of the adhesive interface after TC but also that the resistance of the degradation of each resin cement could also be responsible. This may be a result of the physical properties of Enforce, which have resulted in statistically lower mechanical properties than RelyX ARC, a luting cement considered to be the predecessor of RelyX Ultimate.[58,59] Resin-based materials with lower mechanical properties have been associated with weaker bond strengths.[60] Silva and others[61] showed that Enforce showed greater sorption and solubility when in contact with water in comparison with Relyx ARC. This higher hydrophilicity of Enforce may influence its mechanical properties[62] and, in the end, affect the bond strength of all groups cemented with Enforce when submitted to TC. Future studies need to be done to evaluate the hypothesis tested in the present study but while also comparing the adhesive + resin cement of different manufacturers.

Long-term water storage and thermal fatigue are challenging conditions often used to test the durability of bonding to different substrates.[24,63-65] In the present study, we used 10,000 TC because this method has been estimated to correspond to approximately 1 year of thermal fatigue in the mouth.[63] As dental restorations are expected to last much longer than 1 year in the clinical environment, laboratory studies with longer thermocycling regimens are needed to confirm the results of the present study.

CONCLUSION

The results of the current study indicate that the use of an MDP-containing silane solution or an MDP-containing silane solution associated with an MDP-containing universal adhesive for bonding to air-abraded zirconia results in more stable bonding after thermocycling. The use of a silane solution or adhesive without MDP results in less stable bonding to air-abraded zirconia, mainly after thermocycling.

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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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