Dental Research Journal

Original Article

Effect of 4-META on microtensile bond strength of cements to ceramics

Maliheh Nafisifard[1], Homayoon Alaghehmand[2], Laleh Soleimani[3], Faraneh Mokhtarpour[3]

[1]Dental Materials Research Center, Student Research Committee, Babol University of Medical Sciences, [2]Dental Materials Research Center, Health Research Institute, Babol University of Medical Sciences, [3]Oral Health Research Center, Health Reserch Institute, Babol University of Medical Sciences, Babol, Iran

ABSTRACT

Background: This study assessed the effect of different concentrations of 4-methacryloyloxyethy trimellitate anhydride (4-META) added to silane on microtensile bond strength (μTBS) of light-cure and dual-cure resin cement to hybrid and zirconia-reinforced lithium silicate ceramics.
Materials and Methods: This *in vitro*, experimental study was conducted on 32 Celtra Duo and 32 VITA Enamic ceramics bonded to Allcem Veneer light-cure and Allcem dual-cure resin cements using silane impregnated with 4-META in 0%, 2.5%, 5%, and 10 wt% concentrations in 16 groups (n = 4). The μTBS of specimens was measured by a universal testing machine and analyzed by the Kruskal–Wallis and Mann–Whitney tests, and the mode of failure was determined under a stereomicroscope and analyzed by the Chi-square test (alpha = 0.05).
Results: The lowest mean μTBS was recorded in the Enamic ceramic group with 4-META (0%) bonded to dual-cure cement (14.26 MPa), and the highest mean μTBS was recorded in Enamic ceramic with 4-META (10%) bonded to light-cure cement (18.59 MPa) ($P < 0.001$). The μTBS of Celtra Duo was significantly higher than that of Enamic in bonding to light-cure cement using 4-META (2.5%) ($P = 0.003$). All failures (100%) were adhesive in most groups. The frequency of adhesive failure was the lowest (90%) in Celtra Duo bonded to dual-cure cement with 4-META (5%).
Conclusion: According to the results of this pilot study, the addition of 4-META (10%) to silane caused a significant improvement in μTBS to light-cure cement. The addition of 4-META in all concentrations significantly improved the μTBS to Enamic ceramic in the use of dual-cure cement; however, it had no significant effect on μTBS of Celtra Duo. Nonetheless, the results should be interpreted with caution due to the relatively small sample size.

Key Words: Ceramics, resin cements, silanes, tensile strength

Received: 23-Dec-2022
Revised: 07-Oct-2023
Accepted: 11-Nov-2023
Published: 22-Feb-2024

Address for correspondence:
Dr. Homayoon Alaghehmand,
Dental Materials Research Center, Health Research Institute, Babol University of Medical Sciences, Babol, Iran.
E-mail: halagheh@yahoo

INTRODUCTION

Dental ceramics are the material of choice for many patients requiring esthetic dental restorations due to optimal esthetics, translucency, fluorescence, wear resistance, biocompatibility, and chemical stability.[1] The advent of computer-aided design/computer-aided manufacturing (CAD/CAM) technology enabled the same day delivery of ceramic restorations.[2] Dental

Access this article online

Website: www.drj.ir
www.drjjournal.net
www.ncbi.nlm.nih.gov/pmc/journals/1480

How to cite this article: Nafisifard M, Alaghehmand H, Soleimani L, Mokhtarpour F. Effect of 4-META on microtensile bond strength of cements to ceramics. Dent Res J 2024;21:19.

material manufacturers produce monolithic blocks for chairside CAD/CAM restorations, which are dense and homogeneous, and have minimal internal defects. Chairside CAD/CAM materials can be divided into six groups based on their clinical applications and properties: (I) adhesive ceramics (feldspathic and leucite reinforced) which should be etched and bonded to tooth structure; (II) high-strength ceramics such as lithium disilicate and zirconia-reinforced lithium silicate (ZLS) with improved properties compared with adhesive ceramics; (III) flexible ceramics that do not require a porcelain furnace and are bonded to tooth structure using an adhesive; (IV) composite materials with a resin matrix; (V) full-contour zirconia which is cemented on the tooth; and (VI) provisional materials for provisional restorations.[2]

Celtra Duo is a high-strength ZLS ceramic which has a high content of ultrafine (<1 μm) glass-ceramic crystals and 10% zirconia. It is produced in completely crystalline form by the manufacturer and may be glazed manually or in a ceramic furnace before delivery. It is available in different shades and high and low translucencies. According to the manufacturer, a high number of fine high-glass lithium silicate particles in Celtra Duo is responsible for its excellent optical and mechanical properties, translucency, fluorescence, opalescence, and chameleon effect. It also has optimal marginal adaptation and excellent polishability.[3]

The chairside CAD/CAM blocks of flexible ceramics include LAVA Ultimate, VITA Enamic, and Cerasmart, which have a resin matrix instead of a glass matrix. According to the manufacturers, these ceramics can tolerate higher forces without fracture. Furthermore, they do not require additional heating after fabrication and can be delivered to patients' right away.[4] VITA Enamic is a resin-based hybrid ceramic with 14wt% Triethylene glycol dimethacrylate (TEGDMA) and Urethane dimethacrylate (UDMA). It has an integrated dual structure ceramic network reinforced with leucite and zirconia (86wt%). Its mechanical properties are somewhere between those of glass ceramics and filler-rich composite resins. It also has high wear resistance but is fragile.

Treatment of the bonding surface of ceramics has a significant effect on their clinical service. Treatment of ceramic surfaces is imperative to enhance their adhesion, which can be performed mechanically by sandblasting, hydrofluoric (HF) acid etching, and diamond burs or chemically by the use of silane and bonding agents.[4] Primers are commonly applied to enhance adhesion between dissimilar surfaces. They are substrate specific, and chemical bonding may be obtained to some substrates. Nonetheless, all primers enhance the wettability of bonding surfaces. Silane-based primers are used for metal and ceramic surfaces. Recently, universal primers were introduced which can be applied on various substrates.[5,6]

In the use of both Celtra Duo and Vita Enamic ceramics, the surface is first etched with HF acid (5%–9%), and then the silane coupling agent is applied.[7] Silane coupling agent has a dual function. Its organic functional part reacts with the organic matrix, and its alkoxy groups react with the mineral phase.[8] The silane commonly used in dentistry is the gamma-methacryloxypropyltrim ethoxysilane diluted in ethanol and water, which has a pH of 4–5.[9] Kitahara *et al*.[10] assessed the bond strength of Clearfil ceramic primer containing 10– methacryloyloxydecyl phosphate and single-bottle silane (Clearfil porcelain bond activator) reinforced with 5wt% 4-methacryloyloxyethy trimellitate anhydride (4-META). They reported higher bond strength for silane reinforced with 4-META.[10] It has been reported that after application on the ceramic surface, 4-META is converted to 4-methacryloxyethyl trimellitate due to the effect of surface moisture, and the silane is activated, hydrolyzed, and forms silanol groups, which are bonded to ceramic through the formation of siloxane structure. Furthermore, they showed that silane containing 5wt% 4-META yielded higher shear bond strength compared with silane containing 10wt% 4-META, although this difference did not reach statistical significance.

Appeldoorn *et al*.[11] assessed the shear bond strength of composite to porcelain using All-Bond 2 (Bisco), Cerinate Prime (Den-Mat), Clearfil Porcelain Bond (Kuraray), Etch-Free (Parkell), Monobond-S (Vivadent), Porcelite (Kerr/Sybron), Scotchprime (3M), and Silistor (Kulzer GmbH, Wehrheim, Germany) porcelain repair systems. Without etching, the 4-META bonding agent yielded the highest mean bond strength after 24 h of immersion in water and the second highest mean bond strength after 3 months of water storage. Clearfil Porcelain Bond yielded the highest bond strength after 3 months of water storage.

Both dual-cure and light-cure cement can be used for ceramic bonding. However, previous studies on the effect of the addition of 4-META to silane used dual-cure resin cement, and a comparison between the bond strength of dual-cure and light-cure resin cement to ceramics following the addition of 4-META to silane has not been conducted.[10,12,13]

Considering all the above, this study aimed to assess the effect of the addition of 4-META in 0%, 2.5%, 5%, and 10wt% concentrations to silane on microtensile bond strength (μTBS) of light-cure and dual-cure resin cement to VITA Enamic and Celtra Duo ceramics.

MATERIALS AND METHODS

This *in vitro*, experimental study was conducted on VITA Enamic (VITA, Bad Säckingen, Germany) and Celtra Duo (Sirona Dentsply, Milford, DE, USA) ceramics with Allcem Veneer (FGM, Joinville, SC, Brazil) light-cure and Allcem (FGM, Joinville, SC, Brazil) dual-cure resin cement containing 4-META in 0%, 2.5%, 5%, and 10wt% concentrations in 16 groups (n = 4). Table 1 presents the composition of materials used in this study.

Addition of 4-methacryloyloxyethy trimellitate anhydride to silane

In this study, the Silane Bond Enhancer (Pulpdent, Watertown, USA) was used, which is supplied in 1.2 mL bottles. Thus, 0.03 g of 4-META (Polysciences Erope, Eppelheim, Germany) was weighed by a digital scale (A and D, Tokyo, Japan) and added to the contents of the bottle to obtain silane with 4-META (2.5%). To prepare 4-META (5%), 0.06 g of 4-META was weighed and added to 1.2 mL of silane. To prepare 4-MTA (10%), 0.12 g of 4-META was weighed and added to 1.2 mL of silane. It should be mentioned that after complete mixing of powder with silane, the color of silane solution became transparent with a tint of milky white.

Preparation of study groups

A total of 32 VITA Enamic and 32 Celtra Duo ceramic blocks were selected and manually polished with 600-grit silicon carbide abrasive paper under running water to simulate the internal restoration surface after preparation by bur in a CAD/CAM milling machine.[14] Each group of Enamic and Celtra Duo ceramic blocks was randomly divided into eight subgroups (n = 4) and underwent the following surface treatments:

Groups 1 and 9: The ceramic surfaces were etched with 5% HF acid (prepared by addition of 7 units of distilled water to one unit of 40% HF acid [Merck, Darmstadt, Germany]). The etching time was 30 s for Celtra Duo[15] and 60 s for Enamic blocks.[14] They were then rinsed with water and cleaned in an

Table 1: Composition of materials used in this study

Material	Brand name, manufacturer	Composition
AllCem veneer – light-cure cement	FGM, Joinville, SC, Brazil	Methacrylate monomers, camphorquinone, co-initiators, stabilizers, pigments, silanized barium, aluminum, and silicate glass particles, and silicon dioxide 63% of filler content
AllCem - dual-cure cement	FGM, Joinville, SC, Brazil	Cement base: Methacrylate monomers, camphorquinone, co-initiators, stabilizers, pigments, silanized barium, aluminum, and silicate glass microparticles, and silicon dioxide nanoparticles, inorganic pigments, preservatives Catalyst paste: Methacrylate monomers, dibenzoyl peroxide and stabilizers, barium, aluminum, and silicate glass microparticles 67% of filler content
Vita Enamic	Vita Zahnfabrik, Bad Säckingen, German Dual-network ceramic	86% ceramic (58%–63% SiO_2, 20%–23% Al_2O_3, 9%–11% Na_2O, 4%–6% K_2O, 0%–1% ZrO_2) 14% polymer (UDMA, TEGDMA)
Celtra Duo	Sirona Dentsply, Milford, DE, USA	Zirconium oxide 10.1%, silicon dioxide 58%, lithium oxide 18.5%, phosphorus pentoxide 5%, alumina 1.9%
Merck HF acid 40%	Merck, Darmstadt. Germany liquid 40% HF acid	Chloride: 1 ppm, hexafluorosilicate: 50 ppm, phosphate: 0.5 ppm, sulfate: 2 ppm, arsenic and antimony: 0.03 ppm, silver: 0.020 ppm, aluminum: 0.050 ppm, barium: 0.050 ppm, beryllium: 0.020 ppm, bismuth: 0.020 ppm, calcium: 0.200 ppm
Amber adhesive resin	FGM, Joinville, SC, Brazil	Urethane dimethacrylate resin, HEMA, methacrylate acidic monomers, methacrylate hydrophilic monomers, silanated silicon dioxide, camphorquinone, ethyl 4-dimethylaminobenzoate, ethanol
4-META	Polysciences Erope, Eppelheim, Germany	4-META
Silane-based primer	Pulpdent, Watertown, USA	MPS, 2-propanol

HF: Hydrofluoric, 4META: 4-methacryloyloxyethy trimellitate anhydride; UDMA: Urethane dimethacrylate; TEGDMA: Triethylene glycol dimethacrylate; HEMA: 2-hydroxyethyl methacrylate (HEMA); MPS: 3-Methacryloxyproyltrimethoxysilane (MPS) ultrasonic bath containing 99% alcohol for 5 min and dried with air spray. Silane with 4-META (0%) was applied on the surface by a microbrush, allowed 1 min, and dried with air spray for 15 s. Next, Amber APS (FGM, Joinville, SC, Brazil) bonding agent was applied on the surface, air thinned for 10 s, and light cured for 20 s using a curing unit (Bluephase C8; Ivoclar, Vivadent, Liechtenstein). Allcem Veneer light-cure cement was applied on the bonding agent and ceramic with 0.5 mm thickness as instructed by the manufacturer. Each layer was cured for 20 s. This process was repeated until the thickness of the cement layer reached 4 mm.

The process was the same in other groups with the difference that depending on the group, different concentrations of 4-META and different cement types were used.

Thermocycling

All specimens in all groups underwent 2500 thermal cycles in 5–55°C water baths with 30 s of dwell time and 10 s of transfer time.

Bond strength test

Each block was sectioned into five specimens (a total of 20 in each group) measuring 1 mm × 1 mm using a cutting machine (Delta precision section machine, Mashhad, Iran). The specimens were fixed to the jig of a universal testing machine (TB-5T; Kpppa, Sari, Iran) with cyanoacrylate glue (Razi, Tehran, Iran) and subjected to tensile load at a crosshead speed of 1 mm/min until debonding. The cross-sectional area of specimens at the debonding interface was measured by a digital caliper (Mini Digital Calipers with 100 mm Hold Function; Shinwa Rules Co. Ltd., Sanjo, Japan). The µTBS in megapascals (MPa) was calculated by dividing the load in Newtons by the cross-sectional area in square millimeters.

Mode of failure

The debonding area was inspected under a stereomicroscope (Dewinter Technologies, Milano, Italy) at ×40. The mode of failure was determined as follows:

- Type 1: Cohesive within the ceramic
- Type 2: Cohesive within the cement
- Type 3: Adhesive within the bonding agent
- Type 4: Mixed (a combination of two or more of the above).

Statistical analysis

Data were analyzed by SPSS version 24 (IBM Co., Armonk, NY, USA). Considering the small sample size (presence of four blocks and five sticks in each block and the similarity of the sticks), data were analyzed by the nonparametric Kruskal–Wallis and Mann–Whitney tests. The modes of failures were analyzed by the Chi-square test. $P < 0.05$ was considered statistically significant.

RESULTS

Bond strength

Tables 2 and 3 present the raw data for µTBS of Celtra Duo and Vita Enamic. Table 4 shows the mean µTBS of the groups. As shown, the µTBS of Celtra Duo was significantly higher than that of Enamic in bonding to light-cure cement using 4-META (2.5%) ($P = 0.003$). No other significant difference was noted ($P > 0.05$).

Comparison of µTBS based on different concentrations of 4-META separately for each ceramic type and cement type by the Kruskal–Wallis test revealed a significant difference among Enamic groups with different concentrations of 4-META bonded to dual-cure cement ($P < 0.001$) and light-cure cement ($P = 0.049$). Furthermore, a significant difference was found in the µTBS of Celtra Duo groups with different concentrations of 4-META bonded to dual-cure cement ($P = 0.019$). No other significant differences were noted ($P > 0.05$). Pairwise comparisons of the

Table 2: Raw microtensile bond strength data for Vita Enamic

Vita Enamic	D0%	D2.5%	D5%	D10%	L0%	L2.5%	L5%	L10%
1	23.45	16.75	19.40	16.69	16.75	10.05	13.40	17.20
2	13.40	26.80	14.29	20.89	15.08	10.05	28.47	20.60
3	11.72	13.40	20.37	16.20	16.75	11.72	13.40	27.30
4	11.72	26.18	24.71	25.10	16.75	16.70	16.70	12.22
5	15.07	16.75	13.79	19.24	16.75	18.37	13.40	17.25
6	15.07	13.40	24.00	21.42	21.77	10.05	10.05	18.92
7	12.08	26.80	20.18	22.19	16.75	11.72	21.77	12.22
8	14.30	18.42	15.01	18.18	20.10	12.02	15.07	13.90
9	11.72	12.40	12.29	19.23	23.45	13.75	20.10	16.20
10	13.74	15.40	23.31	20.02	13.40	13.40	16.70	15.57
11	12.93	14.07	16.04	17.83	16.75	21.77	17.17	21.80
12	14.93	14.97	15.80	17.94	10.05	23.05	16.11	21.15
13	13.42	14.54	15.09	16.75	10.11	18.37	15.22	11.77
14	12.7	13.92	14.84	15.92	13.40	19.41	18.25	23.33
15	15.08	16.92	15.42	16.72	12.23	19.70	17.84	21.02
16	12.13	14.75	16.97	17.06	11.04	14.02	15.36	19.20
17	15.92	16.74	15.04	16.91	10.14	12.02	13.14	23.12
18	14.19	15.23	17.13	17.84	11.75	13.20	12.71	18.76
19	15.04	16.07	16.43	16.72	12.14	13.01	13.53	20.67
20	16.75	20.17	17.12	17.86	11.76	15.33	15.34	19.69

D: Dual cure; L: Light cure

Enamic groups (by the Kruskal–Wallis test) with the different concentrations of 4-META bonded to dual-cure cement revealed significant differences between 0% and 2.5% ($P = 0.034$), 0% and 5% ($P = 0.021$), and 0% and 10% ($P = 0.01$) groups, such that the μTBS increased with an increase in concentration of 4-META. No other significant differences were found ($P > 0.05$). Pairwise comparisons of the Enamic groups with the different concentrations of 4-META bonded to light-cure cement revealed significant differences between 0% and 10% ($P = 0.013$) and 2.5% and 10% ($P = 0.01$) groups, such that the μTBS was significantly higher in 4-META (10%). No other significant differences were found ($P > 0.05$).

Comparison of μTBS based on the cement type with different concentrations of 4-META and ceramic type by the Kruskal–Wallis test revealed a significant difference between the μTBS of dual-cure and light-cure groups in the use of 4-MTA (2.5%) for bonding to Celtra Due ceramic, such that the μTBS was significantly higher to light-cure cement ($P = 0.017$). No other significant differences were found ($P > 0.05$).

In comparison of μTBS based on the ceramic type, cement type, and concentration of 4-META, the lowest mean μTBS was recorded in the Enamic ceramic group with 4-MTA (0%) and dual-cure cement (14.26 MPa), and the highest mean μTBS was recorded in Enamic ceramic with 4-META (10%) and light-cure cement (18.59 MPa); this difference was statistically significant as shown by the Kruskal–Wallis test ($P < 0.001$).

Mode of failure

Table 5 presents the frequency of different modes of failure in the four groups. Of 80 Celtra Duo dual-cure specimens, type 3 failure occurred in 77 (93.3%) and type 4 failure occurred in 3 (3.8%) specimens. In each of the Celtra Duo light cure, VITA Enamic dual cure, and VITA Enamic light-cure groups, 78 specimens (97.5%) showed type 3 failure, and 2 specimens (2.5%) showed type 4 failure. Types 1 and 2 were not seen in any group. No significant difference was found among the four groups in the mode of failure ($P = 0.952$).

DISCUSSION

The results showed that the lowest mean μTBS was recorded in Enamic ceramic group with 4-META (0%) and dual-cure cement (14.26 MPa), and the highest mean μTBS was recorded in Enamic ceramic with 4-META (10%) and light-cure cement (18.59 MPa) ($P < 0.001$). A significant difference existed between Celtra Duo and Enamic ceramics in the use of light-cure cement and 4-META (2.5%), such that the μTBS of Celtra Duo was significantly higher than that of Enamic ($P = 0.003$).

Table 3: Raw microtensile bond strength data for Celtra Duo

Celtra Duo	D0%	D2.5%	D5%	D10%	L0%	L2.5%	L5%	L10%
1	28.01	18.37	15.07	16.07	25.12	16.75	13.40	16.75
2	18.42	23.45	15.07	16.14	26.80	16.75	20.10	26.81
3	28.52	20.00	15.00	15.25	10.05	20.10	11.47	21.02
4	15.07	16.07	15.12	17.49	16.75	16.75	13.40	18.00
5	17.07	15.45	18.42	14.63	16.80	20.10	16.75	15.01
6	12.10	12.10	18.42	21.80	18.42	18.42	28.52	18.07
7	12.10	16.00	13.40	19.95	20.10	15.07	18.42	22.00
8	10.02	12.40	16.75	16.02	12.40	20.10	13.45	10.14
9	16.07	13.14	21.77	21.00	22.45	17.04	15.07	13.35
10	12.14	16.07	21.77	18.02	12.04	17.70	21.77	14.82
11	13.78	15.62	19.28	15.00	12.04	15.87	18.01	15.70
12	14.13	18.68	18.02	19.54	11.80	19.41	19.42	12.41
13	14.01	19.41	16.03	18.12	14.12	20.10	15.07	17.42
14	12.40	16.78	15.07	16.71	14.01	25.12	11.77	10.63
15	16.01	15.82	21.77	15.26	16.75	15.42	17.42	11.77
16	16.78	10.06	13.40	11.07	21.02	16.00	18.50	16.80
17	15.41	6.70	15.42	21.33	20.01	17.77	21.04	15.75
18	14.02	14.51	20.11	18.93	12.87	20.02	13.40	18.00
19	13.08	16.07	19.28	19.07	11.05	20.10	20.87	18.03
20	14.33	12.35	19.28	18.92	16.67	17.77	20.87	18.00

D: Dual cure; L: Light cure

Table 4: Mean microtensile bond strength of the groups

Ceramic type	Cement type	4-META, mean±SD (MPa)				*P*
		0%	2.5%	5%	10%	
Celtra Duo	Dual cure	15.67±4.75^{A,a}	15.45±3.73^{A,b}	17.42±2.74^{A,a}	17.51±2.66^{A,a}	0.019
	Light cure	16.56±4.81^{A,a}	18.31±2.36^{A,a}	17.43±4.20^{A,a}	16.52±3.97^{A,a}	0.292
Vita Enamic	Dual cure	14.26±2.62^{A,a}	17.18±4.44^{B,a,b}	17.36±3.50^{B,a}	18.53±2.35^{B,a}	<0.001
	Light cure	14.84±3.91^{A,a}	14.88±3.99^{A,b}	16.18±3.96^{A,B,a}	1859±4.10^{B,a}	0.049
P		0.469	0.004	0.465	0.237	

Uppercase letters show comparisons in rows; lowercase letters show comparisons in columns. SD: Standard deviation; 4META: 4-methacryloyloxyethy trimellitate anhydride

Table 5: Frequency of different modes of failure in the four groups

Group	Type of failure (%)		P*
	4	3	
Celtra Duo dual-cure	77 (93.3)	3 (3.8)	0.952
Celtra Duo light-cure	78 (97.5)	2 (2.5)	
Vita Enamic dual-cure	78 (97.5)	2 (2.5)	
Vita Enamic light-cure	78 (97.5)	2 (2.5)	

*Chi-square test

Kitahara *et al*.[10] reported the bond strength of silane reinforced with 4-META to be equal to that of Clearfil Porcelain Bond Activator + Photo Bond and higher than that of Clearfil Ceramic Primer Plus (Kuraray, Japan), which can be attributed to the conversion of 4-META to 4-MET due to surface moisture and activation of silane, its subsequent hydrolysis, and formation of silanol groups that reinforce the bond strength. Soleimani *et al*.[12] reported an increase in the bond strength of Clearfil Porcelain Bond Activator silane following addition of 4-META under heat treatment. The present results were in agreement with those of the abovementioned two studies. Furthermore, higher bond strength was found in Enamic ceramics cemented with light-cure cement and 4-META (10%) compared with 0% (P = 0.013) and 4-META (10%) compared with 2.5% (P = 0.01). Although the μTBS was also higher in other groups with different concentrations of 4-META compared with 0%, the differences did not reach statistical significance. Unlike the present study, Kitahara *et al*.[10] reported higher microshear bond strength in 4-META (5%) compared with 10%; although this difference was not significant. Such variations can be attributed to the different types of tests and the use of different ceramic types. Chang *et al*.[16] reported that the application of 4-META enhanced the bond strength in general, which was consistent with the present findings.

In the present study, comparison of μTBS based on the cement type in different concentrations of 4-META and ceramic types by the Mann–Whitney test revealed a significant difference between the μTBS of dual-cure and light-cure groups in the use of 4-META (2.5%) for bonding to Celtra Duo ceramic, such that the μTBS was significantly higher in use of light-cure cement (P = 0.017). Furthermore, regarding the mode of failure, the results showed that all failures (100%) were adhesive in most groups. The frequency of adhesive failure was the lowest (90%) in Celtra Duo bonded to dual-cure cement with 4-META (5%).

Asmussen[17] showed that light-cure polymers, especially those cured with visible light, had comparatively high resistance to indentation. This finding was probably due to the relatively fast release of polymerization-initiating radicals from light-cure materials, leading to a high degree of conversion of double bonds. In addition, the low content of inhibitor in light-cure materials may have caused a high proportion of converted double bonds to be engaged in crosslinking of the polymer. The same was reported by Taylor *et al*.[18] Thus, higher frequency of mixed failure in Group 7 can be attributed to lower cross-linking of dual-cure cement and its lower resistance to indentation. Baratto *et al*.[19] reported that cohesive failure was more frequent in the use of dual-cure resin cement, whereas mixed and adhesive failures had a higher frequency in the use of light-cure cement; they reported a significant difference in the mode of failure among the groups. De Carvalho *et al*.[20] demonstrated that mixed failure (adhesive failure between ceramic and cement and cohesive failure within the cement) had the highest frequency.

Comparison of μTBS of Enamic to light-cure cement revealed the highest μTBS in use of 4-META (10%) and the lowest in 4-META (0%). Salz *et al*.[21] showed that increasing the concentration of 4-META in solvent decreased the pKa, and resultantly, the solution became more acidic and its solubility increased. Thus, the enhanced bond strength of Vita Enamic by the addition of 4-META to silane can be attributed to its increased solubility and surface roughness.

Comparison of μTBS of Celtra Duo with light-cure cement revealed the highest μTBS in the use of 4-META (2.5%) and the lowest in 4-META (0%). Abdulkader *et al*.[15] showed that the shear-bond strength of Celtra Duo to resin cement was affected by the type of surface treatment.

Comparison of μTBS based on the type of ceramic, cement, and 4-META concentration revealed that the addition of 4-META to silane caused a significant improvement in μTBS to Enamic ceramic; however, in Celtra Duo groups, no significant difference was noted in any group compared with 4-META (0%). This finding was in line with the results of Straface *et al*.[22] who found that Enamic showed greater surface roughness after HF acid etching compared with other ceramics such as ZLS, and therefore, can provide a potentially greater surface area for the effect of 4-META. Thus, future studies are recommended to assess the surface roughness of these two ceramics immediately after acid etching and before addition of silane using scanning electron microscopy. Bjelopavlovic *et al*.[23] evaluated the retentive strength of Vita Mark II, Empress CAD, e.max CAD, Vita Suprinity, Vita Enamic, and Celtra Duo ceramics and showed that type of ceramic affected the retentive strength, and application of specific materials resulted in higher retentive strength of some ceramic types.

In response to the question of whether silane coupling agent is imperative for bonding of ceramic to resin, it should be mentioned that mixing of silane with an acidic agent or its heating right before application is imperative for its activation. Thus, the conventional silane coupling agents are mixed with bonding agents containing acidic monomers for simplified application. According to Kitahara *et al*.,[10] 4-META converts to 4-MET in the presence of moisture, and the hydrolysis of silane molecules is enhanced by the creation of an acidic environment with a pH of 3.

In the present study, the addition of 4-META (10%) to silane in bonding of VITA Enamic to light-cure cement caused a significant improvement in bond strength; the increase in bond strength was significant in addition of all concentrations of 4-META to silane in bonding to dual-cure cement. Thus, minimum (2.5%) concentration of 4-META can be used in the application of dual-cure cement, and 4-META (10%) can be used in the application of light-cure cement for bonding to VITA Enamic ceramic to enhance the bond strength. This finding was in line with the results of Soleimani *et al*.,[12] who recommended the addition of 4-META to silane. Considering the higher stiffness of Celtra Duo ceramic compared with Enamic,[24] lower bond strength of Celtra Duo can be attributed to the formation of more defects during sectioning with diamond discs.[25] Furthermore, considering the higher surface roughness of Enamic[22] compared with Celtra Duo after acid etching with HF acid and dissolution of glass phase, it may be concluded that the application of 4-META on the Enamic ceramic affects the bond to the ceramic phase at a greater depth, and the micromechanical bond of polymer phase and resin cement would lead to greater effect of 4-META on Enamic, compared with Celtra Duo.

This study had an *in vitro* design. Thus, the generalization of results to the clinical setting must be done with caution. Further studies are required on the shelf-life of silane containing 4-META.

CONCLUSION

According to the results of this pilot study, the addition of 4-META (10%) to silane caused a significant improvement in µTBS to light-cure cement. The addition of 4-META in all concentrations significantly improved the µTBS to Enamic ceramic in the use of dual-cure cement; however, it had no significant effect on µTBS of Celtra Duo. Nonetheless, the results should be interpreted with caution due to the relatively small sample size.

Financial support and sponsorship
Nil.

Conflicts of interest
The authors of this manuscript declare that they have no conflicts of interest, real or perceived, financial or non-financial in this article.

REFERENCES

1. Gomes EA. Ceramic in dentistry: Current situation. Cerâmica 2008;54:319-25.
2. Kelly JR, Nishimura I, Campbell SD. Ceramics in dentistry: historical roots and current perspectives. J Prosthet Dent 1996;75:18-32.
3. Chavali R, Nejat AH, Lawson NC. Machinability of CAD-CAM materials. J Prosthet Dent 2017;118:194-9.
4. Cekic-Nagas I, Ergun G, Egilmez F, Vallittu PK, Lassila LV. Micro-shear bond strength of different resin cements to ceramic/glass-polymer CAD-CAM block materials. J Prosthodont Res 2016;60:265-73.
5. Lung CYK, Matinlinna JP. Aspects of silane coupling agents and surface conditioning in dentistry: An overview. Dent Mater 2012;28:467-77.
6. Matinlinna JP, Lassila LV, Ozcan M, Yli-Urpo A, Vallittu PK. An introduction to silanes and their clinical applications in dentistry. Int J Prosthodont 2004;17:155-64.
7. Peumans M, Valjakova EB, De Munck J, Mishevska CB, Van Meerbeek B. Bonding effectiveness of luting composites to different CAD/CAM materials. J Adhes Dent 2016;18:289-302.
8. D'Arcangelo C, D'Amario M, De Angelis F, Zazzeroni S, Vadini M, Caputi S. Effect of application technique of luting agent on the retention of three types of fiber-reinforced post systems. J Endod 2007;33:1378-82.
9. Perdigão J, Gomes G, Lee IK. The effect of silane on the bond strengths of fiber posts. Dent Mater 2006;22:752-8.
10. Kitahara N, Itoh K, Kusunoki M, Oikawa M, Miyazaki T. One-bottle silane coupling agent containing 4-META. Dent Mater J 2013;32:409-12.
11. Appeldoorn RE, Wilwerding TM, Barkmeier WW. Bond strength of composite resin to porcelain with newer generation porcelain repair systems. J Prosthodont 1993;2:215-9.
12. Soleimani L, Alaghemand H, Fatemi SM, Esmaeili B. Effect of heat treatment and addition of 4-META to silane on microtensile

bond strength of IPS e. max CAD ceramic to resin cement. Dent Res J 2019;16:318-26.
13. Yazarloo F, Alaghehmand H, Mokhtarpour F. Effect of hydrofluoric acid concentration and etching time on microtensile bond strength of suprinity and enamic CAD/CAM ceramics to resin cement. Caspian J Dent Res 2019;8:16-23.
14. Lauvahutanon S, Takahashi H, Shiozawa M, Iwasaki N, Asakawa Y, Oki M, *et al*. Mechanical properties of composite resin blocks for CAD/CAM. Dent Mater J 2014;33:705-10.
15. Abdulkader KF, Elnaggar GA, Kheiralla LS. Shear bond strength of cemented zirconia-reinforced lithium silicate ceramics (Celtra Duo) with two surface treatments (*in vitro* study). J Adhes Sci Technol 2021;35:35-51.
16. Chang J, Scherer W, Tauk A, Martini R. Shear bond strength of a 4-META adhesive system. J Prosthet Dent 1992;67:42-5.
17. Asmussen E. Restorative resins: Hardness and strength versus quantity of remaining double bonds. Scand J Dent Res 1982;90:484-9.
18. Taylor P, Avérous L, Ave L. Biodegradable multiphase systems based on plasticized starch: A review. J Macromol Sci Part C Polym Rev 2007;14:37-41.
19. Baratto SS, Spina DR, Gonzaga CC, Cunha LF, Furuse AY, Baratto Filho F, *et al*. Silanated surface treatment: Effects on the bond strength to lithium disilicate glass-ceramic. Braz Dent J 2015;26:474-7.
20. de Carvalho RF, Martins ME, de Queiroz JR, Leite FP, Ozcan M. Influence of silane heat treatment on bond strength of resin cement to a feldspathic ceramic. Dent Mater J 2011;30:392-7.
21. Salz U, Mücke A, Zimmermann J, Tay FR, Pashley DH. pKa value and buffering capacity of acidic monomers commonly used in self-etching primers. J Adhes Dent 2006;8:143-50.
22. Straface A, Rupp L, Gintaute A, Fischer J, Zitzmann NU, Rohr N. HF etching of CAD/CAM materials: Influence of HF concentration and etching time on shear bond strength. Head Face Med 2019;15:1-10.
23. Bjelopavlovic M, Weyhrauch M, Scheller H, Wentaschek S, Lehmann KM. Retentive strength of CAD/CAM-fabricated all-ceramic crowns luted on titanium implant abutments using different ceramic materials and luting agents: An *in vitro* study. Materials (Basel) 2022;15:6968.
24. Lawson NC, Bansal R, Burgess JO. Wear, strength, modulus and hardness of CAD/CAM restorative materials. Dent Mater 2016;32:e275-83.
25. Sakaguchi RL, Powers JM. Craig's Restorative Dental Materials-E-Book. St.Louis Misso: Elsevier Health Sciences; 2012. p. 322.