Bonding Effectiveness of Luting Composites to Different CAD/CAM Materials

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Purpose: To evaluate the influence of different surface treatments of six novel CAD/CAM materials on the bonding effectiveness of two luting composites.

Materials and Methods: Six different CAD/CAM materials were tested: four ceramics – Vita Mark II; IPS Empress CAD and IPS e.max CAD; Celtra Duo – one hybrid ceramic, Vita Enamic, and one composite CAD/CAM block, Lava Ultimate. A total of 60 blocks (10 per material) received various mechanical surface treatments: 1. 600-grit SiC paper; 2. sandblasting with 30-µm Al_2O_3; 3. tribochemical silica coating (CoJet). Subsequent chemical surface treatments involved either no further treatment (control), HF acid etching (HF), silanization (S, or HF acid etching followed by silanization (HF+S). Two specimens with the same surface treatment were bonded together using two dual-curing luting composites: Clearfil Esthetic Cement (self-etching) or Panavia SA Cement (self-adhesive). After 1 week of water storage, the microtensile bond strength of the sectioned microspecimens was measured and the failure mode was evaluated.

Results: The bonding performance of the six CAD/CAM materials was significantly influenced by surface treatment (linear mixed models, $p < 0.05$). The luting cement had a significant influence on bond strength for Celtra Duo and Lava Ultimate (linear mixed models, $p < 0.05$). Mechanical surface treatment significantly influenced the bond strength for Celtra Duo ($p = 0.0117$), IPS e.max CAD ($p = 0.0115$), and Lava Ultimate ($p < 0.0001$). Different chemical surface treatments resulted in the highest bond strengths for the six CAD/CAM materials: Vita Mark II and IPS Empress CAD: S, HF+S; Celtra Duo: HF, HF+S; IPS e.max CAD: HF+S; Vita Enamic: HF+S, S. For Lava Ultimate, the highest bond strengths were obtained with HF, S, HF+S. Failure analysis showed a relation between bond strength and failure type: more mixed failures were observed with higher bond strengths. Mainly adhesive failures were noticed if no further surface treatment was done. The percentage of adhesive failures was higher for CAD/CAM materials with higher flexural strength (Celtra Duo, IPS e.max CAD, and Lava Ultimate).

Conclusion: The bond strength of luting composites to novel CAD/CAM materials is influenced by surface treatment. For each luting composite, an adhesive cementation protocol can be specified in order to obtain the highest bond to the individual CAD/CAM materials.

Keywords: CAD/CAM block, composite cement, microtensile bond strength, surface treatment.

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In restorative dentistry today, computerized techniques have made great progress and are becoming commonplace. Digital systems allow 3D modeling and chairside milling of restorations. Cerec, the most well-known and studied CAD/CAM system, enables the manufacture of restorations in a single appointment.[24,25] The tooth is prepared, an optical impression is made, the restoration is designed on the computer and milled out of a CAD/CAM block, and finally bonded to the tooth. Research into and production of materials suitable for CAD/CAM restorations is one of the

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Table 1 General composition of materials tested in this study

Product name (manufacturer)		Composition*
CAD/CAM block	Celtra Duo (Dentsply; Konstanz, Germany)	SiO_2, Li_2O, ZrO_2, P_2O_5, Al_2O_3, K_2O, CeO_2, pigments
	IPS Empress CAD (Ivoclar Vivadent; Schaan, Liechtenstein)	SiO_2, Al_2O_3, K_2O, Na_2O, BaO, CaO, CeO_2, B_2O_3, TiO_2, pigments
	IPS e.max CAD (Ivoclar Vivadent)	SiO_2, Li_2O, K_2O, P_2O_5, ZrO_2, ZnO, Al_2O_3, MgO, pigments
	Lava Ultimate (3M ESPE)	SiO_2, ZrO_2, bis-GMA, UDMA, bis-EMA, TEG-DMA
	Vita Enamic (Vita Zahnfabrik; Bad Säckingen, Germany)	SiO_2, Al_2O_3, Na_2O, K_2O, B_2O_3, CaO, TiO_2, TEG-DMA, UDMA
	Vita Mark II (Vita Zahnfabrik)	SiO_2, Al_2O_3, Na_2O, K_2O, CaO, TiO_2, pigments
Composite cement	Clearfil Esthetic Cement (Kuraray Noritake; Okayama, Japan)	Paste A: bis-GMA, TEG-DMA, hydrophobic aromatic dimethacrylate, silanated barium glass filler, colloidal silica Paste B: bis-GMA, TEG-DMA, hydrophobic aromatic dimethacrylate, hydrophilic aliphatic dimethracrylate, silanated barium glass filler, silanated silica, colloidal silica, catalysts, dl-camphorquinone, pigments
	Panavia Self-adhesive Cement (Kuraray Noritake)	Paste A: 10-MDP, bis-GMA, TEG-DMA, hydrophobic aromatic dimethacrylate, silanated barium glass filler, silanated colloidal silica, dl-camphorquinone, benzoyl peroxide, initiators Paste B: bis-GMA, hydrophobic aromatic dimethacrylate, hydrophobic aliphatic dimethracrylate, silanated barium glass filler, silanated colloidal silica, surface treated sodium fluoride, accelerators, pigments
Surface treatment	Aluminum oxide (Danville; Zürich, Switzerland)	Al_2O_3 (27 µm)
	CoJet (3M ESPE)	SiO_2-coated Al_2O_3 (30 µm)
	IPS Ceramic Etching Gel (Ivoclar Vivadent)	HF acid <5%
	Monobond Plus (Ivoclar Vivadent)	Ethanol, 3-methoxysilylpropyl methacrylate, phosphoric acid methacrylate, sulphide methacrylate
	Heliobond (Ivoclar Vivadent)	Bis-GMA, TEG-DMA

*According to the information from the manufacturers' official websites. 10-MDP: 10-methacryloyloxydecyl dihydrogen phosphate; bis-EMA: ethoxylated bisphenol-A dimethacrylate; bis-GMA: bisphenol A diglycidylmethacrylate; TEG-DMA: triethyleneglycol dimethacrylate; UDMA: urethane dimethacrylate.

fastest-growing and changing fields in dental materials. Most CAD/CAM blocks used for fabrication of indirectly bonded tooth-colored restorations are made of glass ceramics: feldspar ceramic, leucite reinforced glass ceramic, lithium disilicate glass, and zirconium-reinforced lithium silicate glass ceramics.[21,45] Advantages of glass ceramics are their strength and superior optical properties. However, they are stiff, brittle materials, with low fracture toughness and high susceptibility to fracture.[11,36,44] This is less pronounced for lithium disilicate glass ceramics.[1,8,20] To overcome the shortcomings of glass ceramics, so-called hybrid ceramics and composite blocks with dispersed fillers have been introduced.[1,23,36] Hybrid ceramics are defined as a material consisting of a ceramic substructure infiltrated with a polymer network. The attractiveness of both materials is based on ease of fabrication and milling.[28,34] These materials may be less susceptible to chipping during the milling procedure,[42] resulting in better marginal adaptation.[1,5] The staining and glazing procedure is easier. Intraoral repair of minor defects is more straightforward as well. Finally, in comparison with direct composite materials, they have more favorable physicomechanical properties.[1,23]

Composite resin bonding is a crucial step in the process of placing indirect restorations that rely on adhesion, such as tooth-colored indirect onlays/partial crowns/crowns, and is indispensable for their longevity. The characteristics of a

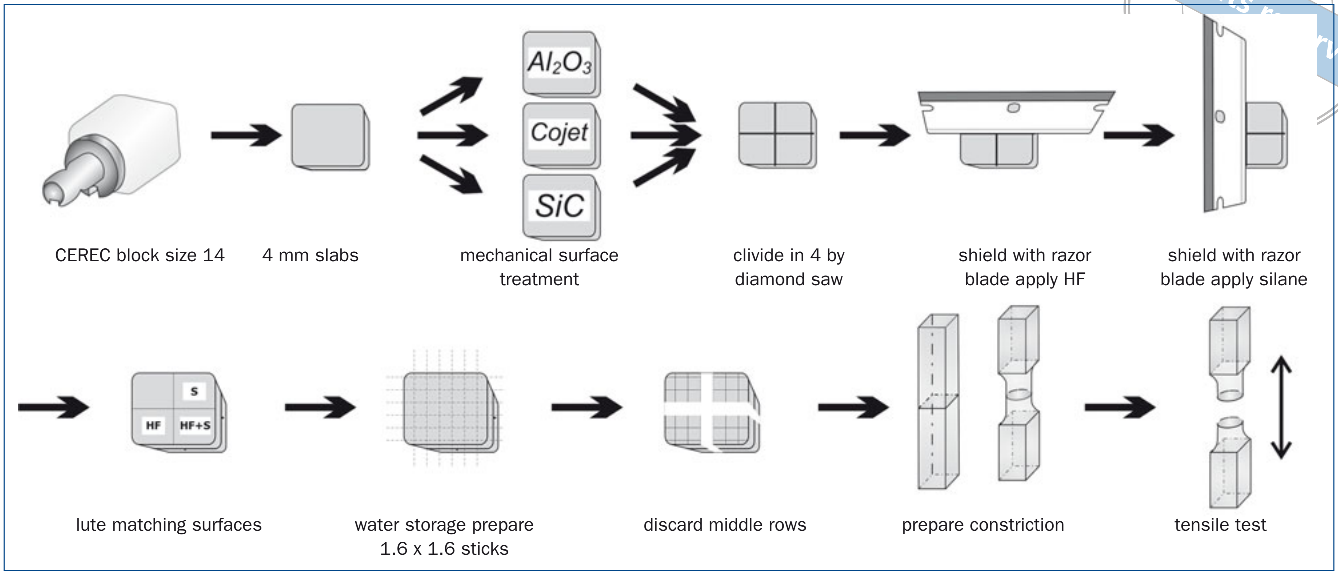

Fig 1 Schematic presentation of the specimen preparation design.

resilient and durable adhesive bond are high retention, prevention of microleakage, and enhancement of marginal adaptation. Furthermore, successful adhesive bonding can increase fracture resistance of the restored tooth and the indirect restoration.[3,8,12,19] Although the bonding effectiveness between luting composites and the tooth surface has been well researched, scientific evidence on bonding behavior of different luting composites and surface treatment of the new CAD/CAM materials is scarce. Independent studies that investigate resin bond strength and preferred treatment protocols for this new and increasingly popular materials group are needed. Therefore, the aim of present study was to evaluate the effect of different surface treatments on microtensile bond strength of two different luting composites to six novel CAD/CAM materials.

MATERIALS AND METHODS

Six CAD/CAM materials and two luting composites were used. Four of the CAD/CAM materials were ceramics: Vita Mark II (Vita Zahnfabrik; Bad Säckingen, Germany), IPS Empress CAD, IPS e.max CAD (Ivoclar Vivadent; Schaan, Liechtenstein); Celtra Duo (Dentsply; Konstanz, Germany). One was a hybrid ceramic block, Vita Enamic (Vita Zahnfabrik), and one a composite block, Lava Ultimate (3M ESPE; Neuss, Germany). Panavia SA Cement (self-adhesive) and Clearfil Esthetic Cement (self-etching) were the dual-curing luting composites (Kuraray Noritake; Okayama, Japan). Table 1 lists manufacturers and compositions of the materials used.

Grouping of Specimens

Ceramic sections (12 x 14 x 5.45 mm) were obtained from 6 different CAD/CAM blocks (Table 1) with a diamond blade (diamond sectioning wheel M1D10, Struers; Ballerup, Denmark). For each material, 10 CAD/CAM blocks were used.

A schematic illustration of specimen preparation is shown in Fig 1. The cementation surfaces of all ceramic sections were ground flat for surface standardization with 320- and 600-grit silicon-carbide (SiC) abrasive paper (Buehler; Düsseldorf, Germany) in a polishing machine (Buehler Beta) under continuous water cooling. They were then cut into 4 sections with a diamond blade. All ceramic sections were ultrasonically cleaned in distilled water for 10 min to remove any surface contaminants, and then air dried. All sections were randomly divided into 3 groups according to surface treatment (two blocks per surface treatment per CAD/CAM material per luting cement) (Table 2): SiC: no further treatment (= control); 2. Al_2O_3: sandblasted with 27-μm Al_2O_3 particles (Danville Materials; Zürich, Switzerland); 3. CoJet: tribochemical silica coating, ie, sandblasting with 30-μm Al_2O_3 particles modified with silica (CoJet, 3M ESPE; Seefeld, Germany).

A razor blade was used to divide the ceramic surface in quarters depending on the subsequent treatment (Fig 1):

- No further treatment.
- HF: the surface was etched with 5% hydrofluoric acid (HF) gel (IPS Ceramic Etching Gel, Ivoclar Vivadent). The etching time differs for each ceramic type according to the instructions of the respective manufacturer (Table 2).
- S: Silane (Monobond Plus, Ivoclar Vivadent) was applied in a thin coat and allowed to react for 60 s.
- HF+S: HF acid etching and silanization (combination of 2 + 3).

The surfaces were covered with liquid, unfilled bonding resin (Heliobond, Ivoclar Vivadent) that was not light cured.

Table 2 Application procedure of the different mechanical and chemical surface treatments

	Product name (manufacturer)	Application procedure	Procedure after treatment
Mechanical surface treatment	SiC abrasive paper (Buehler; Düsseldorf, Germany)	Ground flat until homogenous surface was obtained	Specimens were ultrasonically cleaned in distilled water for 10 min to remove all particles and debris, then air dried.
	Aluminum oxide (Danville; Zürich, Switzerland)	Blasting perpendicular to the surface, distance: 10 mm, time: 20 s, pressure: 2.8 bars	Specimens were ultrasonically cleaned in distilled water for 5 min to remove all particles and debris, then air dried.
	CoJet (3M ESPE; Neuss, Germany)		Surfaces were cleaned with soft air blowing for 5 s.
Chemical surface treatment	IPS Ceramic Etching Gel (Ivoclar Vivadent; Schaan, Liechtenstein)	Celtra Duo: 30 s IPS Empress CAD: 60 s IPS e.max CAD: 20 s Lava Ultimate: 60 s Vita Mark II: 60 s Vita Enamic: 60 s	Surfaces were thoroughly rinsed with water for 60 s to remove residual acid (the etching gel was rinsed with water for 5 min in a polyethylene cup containing a spoonful of powder of calcium carbonate $CaCO_3$ and sodium carbonate Na_2CO_3 to neutralize Hf). The etched surfaces were air dried with compressed air.
	Monobond Plus (Ivoclar Vivadent)	Applied in a thin coat, reaction time: 60 s	Any remaining excess was dispersed with a gentle stream of air to induce further evaporation of the solvent.
	Heliobond (Ivoclar Vivadent)	Applied in a thin coat	Excess bonding resin was air thinned. Heliobond was not light cured.

Luting Procedure

After surface treatment, two ceramic blocks having received the same surface treatment were luted together (sandwich block) with one of the two dual-curing composite cements, Clearfil Esthetic Cement or Panavia SA Cement, with a constant load of 1 kg for 10 min and the interface oriented perpendicular to the vertical load. The composite cement was left to set in primarily self-curing mode for the first 2 min (in ambient room light), thereby simulating the average time clinically needed for luting prior to actual light curing. Next, the cement was light cured for 40 s from each of the four sides of the block, parallel to the cement interface, to ensure optimal polymerization with a polywave high-power LED light curing unit (Biophase 20i, Ivoclar Vivadent) in high-power mode with an approximate output (light intensity) of 1000 mW/cm^2. The light output was checked regularly. After 10 min, the specimens were removed from the press, and additionally polymerized for an extra 60 s on each of the four sides of the block. In total, the cement was light cured for 100 s x 4 sides = 400 s (approx. 7 min). The blocks were stored in distilled water at 37°C for 24 h prior to microspecimen preparation.

Microtensile Bond Strength Test

The blocks were fixed to the custom-adapted support, which was mounted in a precision cutting machine (Accutom 50, Struers). Slices were obtained with a slow-speed (3000 to 4000 rpm, 0.020 to 0.070 mm/s) diamond disk with a thickness of 0.30 mm (Struers, Denmark) under permanent water cooling, starting at the top surface of the block, through the ceramics, and perpendicular to the cement interface. The grooves were cut until 1 mm remained at the bottom. The slabs were thus fixed in position. The block of slabs (support) was then rotated by 90 degrees and cut again, perpendicular to the cement interface to yield rectangular microbars of 1.6 x 1.6 mm width and 10 mm length (adhesive area of about 2.56 mm^2). The outer microbars of each block as well as those near the grooves were discarded because the results could have been affected by luting defects at the cement interface. Only the internal samples were used. Next, all microbars were trimmed at the cement interface to a cylindrical dumbbell shape with an isthmus diameter of about 1.1 mm using the MicroSpecimen Former (University of Iowa; Iowa City, IA, USA) equipped with a fine cylindrical diamond bur (8882 314 014, Komet, Gebr. Brasseler; Lemgo, Germany) under continuous air-water spray. The cross-sectional diameter was precisely measured (accuracy of 0.001 mm) with a precision-measuring instrument transformed from an X-Y-Z multipurpose modular microscope (Ernst Leitz; Wetzlar, Germany).

The microspecimens were stored in distilled water at 37°C for 1 week, after which a µTBS test was conducted. For that purpose, the ends of each microbar were fixed to a BIOMAT jig with cyanoacrylate glue (Model Repair II Blue, Dentsply). The jig was fixed into a universal testing machine (LRX material testing device, Lloyd Instruments; Fareham, Hampshire, UK), and stressed under tensile force until failure at a crosshead speed of 1 mm/min. The µTBS was expressed in MPa, derived by dividing the imposed force (N) at the time of fracture by the bonded area (mm^2) (MPa = N/mm^2). If specimens failed before the actual testing (pre-test failures, ptf), the µTBS was recorded as zero and included in subsequent statistical analyses. An explicit note was made of the number of ptfs.

The mode of failure/fracture (adhesive, mixed, cohesive in ceramic) for each beam was determined using light microscopy at a magnification of 50X with a stereomicroscope (Stemi 2000-CS, Carl Zeiss; Oberkochen, Germany).

Statistical Analysis

Microtensile bond strength data (µTBS per microspecimen in MPa) were statistically analyzed using a linear mixed effects model. For each type of CAD/CAM block, a separate statistical model was constructed including the following fixed factors: surface preparation (Al_2O_3, CoJet or SiC), the application of silane (yes or no), the application of HF (yes or no) and the luting cement (Clearfil Esthetic Cement or Panavia SA Cement), along with their first-order interactions. The CAD/CAM block from which each beam originated was included in the model as a random effect. For each statistical model, the groups with the highest bond strength for each cement were identified, and a 95% confidence interval was calculated. Groups with a mean inside this interval were considered not statistically different from the best-performing group. All tests were performed at a significance level of $\alpha = 0.05$ using a statistical software package (R 3.1.1 and nlme package, R Foundation for Statistical Computing; Vienna, Austria).

RESULTS

The µTBS results for the six CAD/CAM materials and two luting cements after different surface treatments are recorded in Fig 2 (A-F). Tables 3 and 4 show the results of the statistical analysis (linear mixed effects model). The failure analysis for the six CAD/CAM materials is presented in Fig 3 (A-F).

IPS Empress CAD and Vita Mark II

The application of S was necessary to obtain the highest bond strengths for both types of ceramic blocks ($p < 0.001$; Vita Mark II: 38.5 MPa; IPS Empress CAD: 41.3 MPa; $p < 0.001$). The application of HF also improved µTBS ($p < 0.0001$), but to a lesser extent (IPS Empress CAD: 24.2 MPa; Vita Mark II: 25.3 MPa). No additional benefit was recorded when HF acid etching was combined with application of S (Empress CAD: 35.9 MPa; Vita Mark II: 32.5 MPa; $p < 0.0001$). Mechanical surface preparation with Al_2O_3 or CoJet did not significantly increase bond strengths to either CAD/CAM materials: Vita Mark II – Al_2O_3: 22.5 MPa; CoJet: 23.7 MPa; SiC: 26.5 MPa; $p = 0.574$; IPS Empress CAD – Al_2O_3: 29.5 MPa; CoJet: 23.9 MPa; SiC: 23.1 MPa; $p = 0.084$. For IPS Empress CAD in combination with Clearfil Esthetic Cement, however, all SiC groups showed significantly lower bond strengths than the best performing Al_2O_3 (S, HF+S) and CoJet groups (S) ($p = 0.04$) (Figs 2C and 2D, Tables 3 and 4).

Celtra Duo

All the best pretreatment protocols for Celtra Duo included etching with HF acid (41.5 MPa; $p < 0.0001$). An additional application of S did not yield any benefit in terms of short-term µTBS (38.51 MPa) ($p = 0.0005$). A small but significant ($p = 0.0117$) benefit of mechanical surface preparation with Al_2O_3 or CoJet was recorded (SiC: 21.7 MPa; Al_2O_3: 23 MPa; CoJet: 22.4 MPa). The luting cement also had a significant influence on bond strength for Celtra Duo, with Clearfil Esthetic Cement (27.9 MPa) showing higher bond strengths than Panavia SA Cement (16.8 MPa) ($p = 0.0012$).

IPS e.max CAD

Bond strengths for IPS e.max CAD were unambiguous. Application of HF (27.1 MPa) and silane (19.8 MPa) both significantly ($p < 0.0001$) increased the µTBS (50.3 MPa; $p < 0.0001$), and these effects were additive, as no interaction between these factors was observed ($p = 0.1553$). Here, too, surface preparation by Al_2O_3 or CoJet resulted in a small increase in µTBS (SiC: 20.2 MPa; CoJet: 29 MPa; Al_2O_3: 23.20 MPa; $p = 0.0115$). µTBS with Clearfil Esthetic Cement was slightly higher than with Panavia SAC. However, the difference was not statistically significant (29.4 MPa vs 18.9 MPa, $p = 0.0979$).

Vita Enamic

This was the CAD/CAM block type with the highest number of groups (12) not significantly different from the best one. All groups including a pretreatment with silane were not significantly different from the best group (44.9 MPa; $p < 0.0001$). Nevertheless, a small benefit was observed with the combination of HF and S (46.3 MPa; $p = 0.0024$). It is noteworthy that Vita Enamic was the only block in which there were no pre-test failures in any group. Even the groups with neither mechanical nor chemical pretreatment showed moderate bond strength (13.5 MPa). In addition, no significant differences were recorded between the different mechanical surface treatments (SiC: 33.9 MPa; CoJet: 36.7 MPa; Al_2O_3: 37.8 MPa; $p = 0.223$).

Lava Ultimate

For this composite block, many pretreatments also resulted in high µTBS. The most influential parameter was mechanical pretreatment (Al_2O_3: 50.1 MPa; CoJet: 45 MPa; SiC: 33.5 MPa; $p < 0.0001$). All protocols including Al_2O_3 or CoJet showed µTBS values higher than 29 MPa. Nevertheless, an additional application of silane increased µTBS significantly (41.5 MPa; $p = 0.0015$). The same observation was made after HF acid etching (50.4 MPa; $p < 0.0001$). However, no additional benefit was recorded when HF and S were combined (49.7 MPa; $p < 0.001$). Regarding the luting cement, significantly higher bond strengths were observed for Panavia SA Cement than for Clearfil Esthetic Cement (40.6 MPa vs 44.9 MPa; $p < 0.0001$).

Regarding failure analysis, the percentage of mixed failures within a group (CAD/CAM material, luting composite) was higher when higher bond strengths were obtained

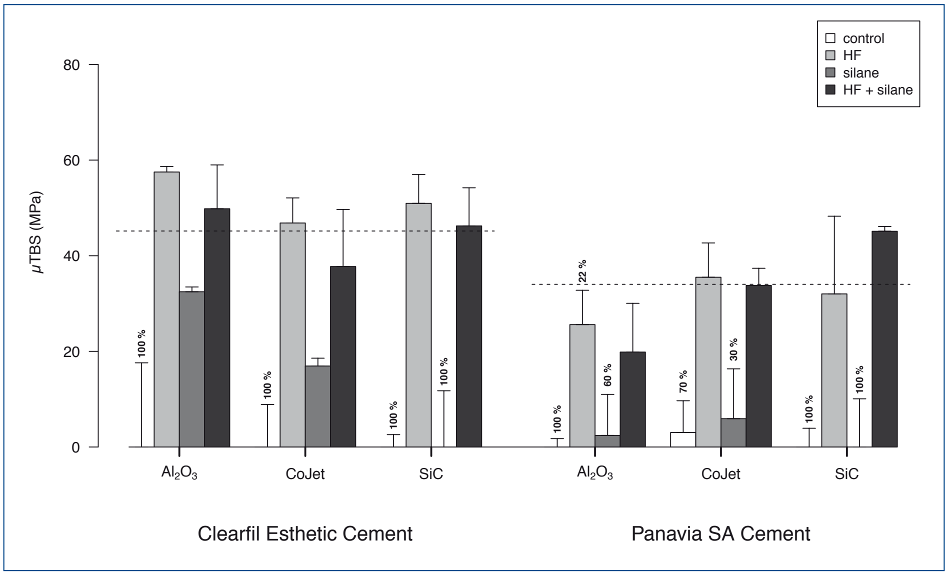

Fig 2A Bar graph of the mean μTBS (in MPa) for Celtra Duo. Whiskers extend to the 95% confidence intervals as calculated from the respective linear mixed effects model. The dotted line represents the lower confidence limit of the best performing group; bars below this line are considered inferior to the best performing group. If pre-test failures occurred, the percentage of pre-test failures is given above the bar.

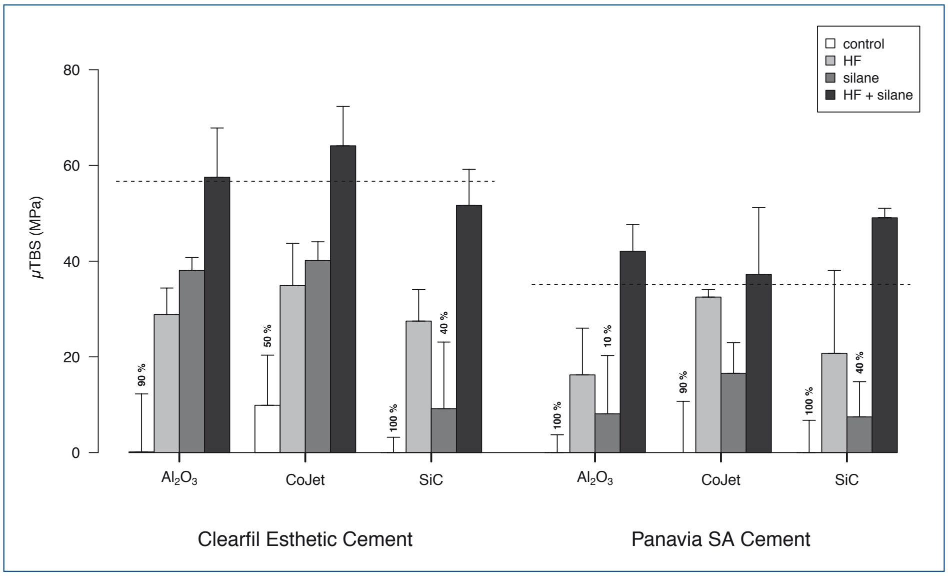

Fig 2B Bar graph of the mean μTBS (in MPa) for IPS e.max CAD. Whiskers extend to the 95% confidence intervals as calculated from the respective linear mixed effects model. The dotted line represents the lower confidence limit of the best performing group; bars below this line are considered inferior to the best performing group. If pre-test failures occurred, the percentage of pre-test failures is given above the bar.

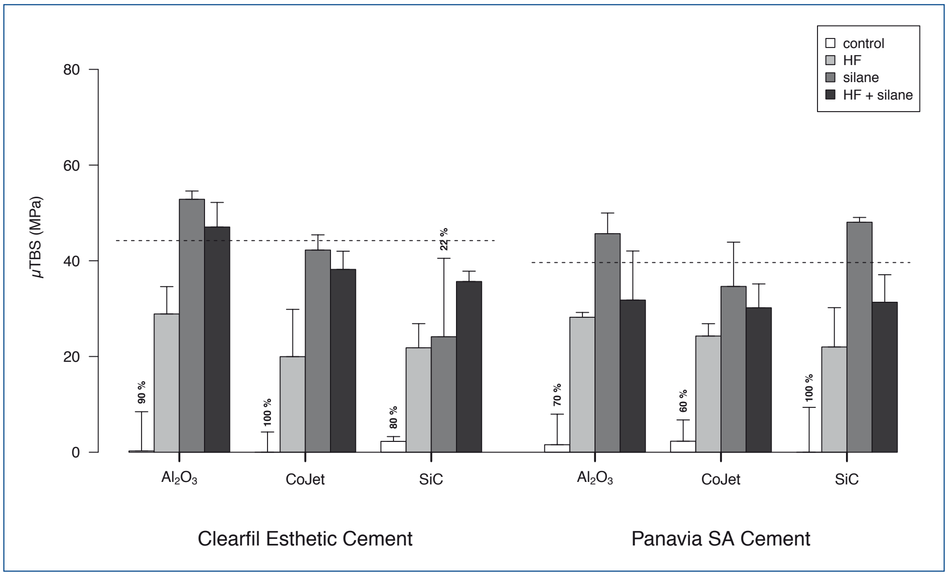

Fig 2C Bar graph of the mean μTBS (in MPa) for IPS Empress CAD. Whiskers extend to the 95% confidence intervals as calculated from the respective linear mixed effects model. The dotted line represents the lower confidence limit of the best performing group; bars below this line are considered inferior to the best performing group. If pre-test failures occurred, the percentage of pre-test failures is given above the bar.

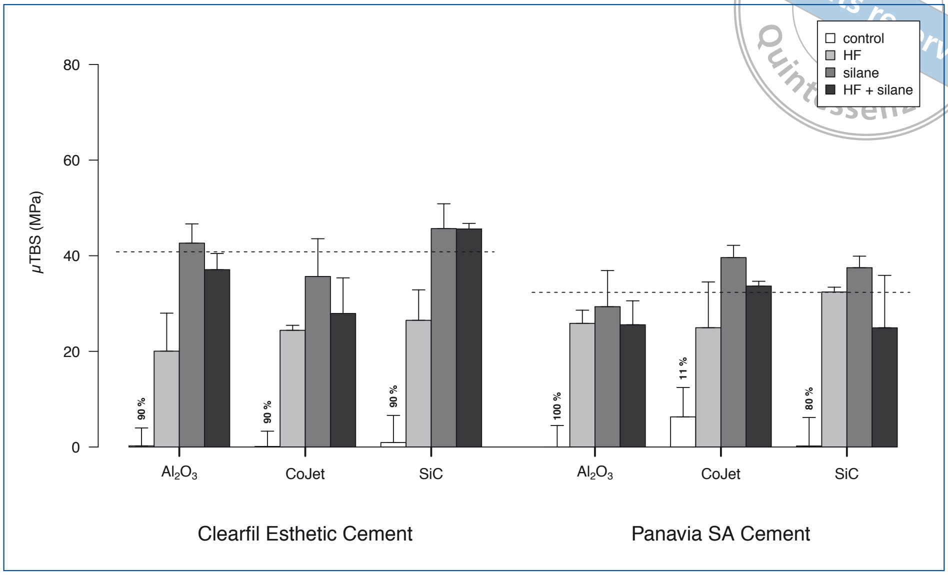

Fig 2D Bar graph of the mean μTBS (in MPa) for Vitablocs Mark II. Whiskers extend to the 95% confidence intervals as calculated from the respective linear mixed effects model. The dotted line represents the lower confidence limit of the best performing group; bars below this line are considered inferior to the best performing group. If pre-test failures occurred, the percentage of pre-test failures is given above the bar.

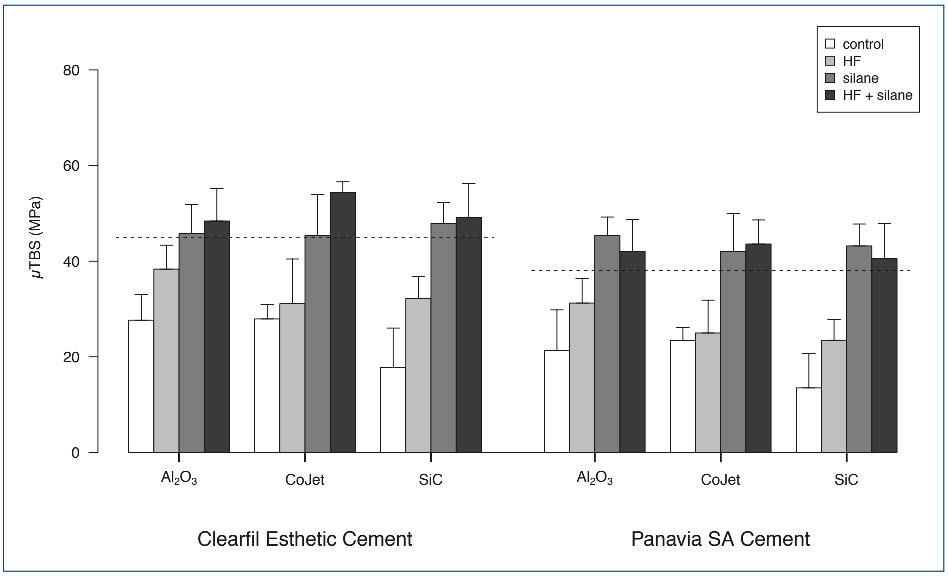

Fig 2E Bar graph of the mean μTBS (in MPa) for Vita Enamic. Whiskers extend to the 95% confidence intervals as calculated from the respective linear mixed effects model. The dotted line represents the lower confidence limit of the best performing group; bars below this line are considered inferior to the best performing group. If pre-test failures occurred, the percentage of pre-test failures is given above the bar.

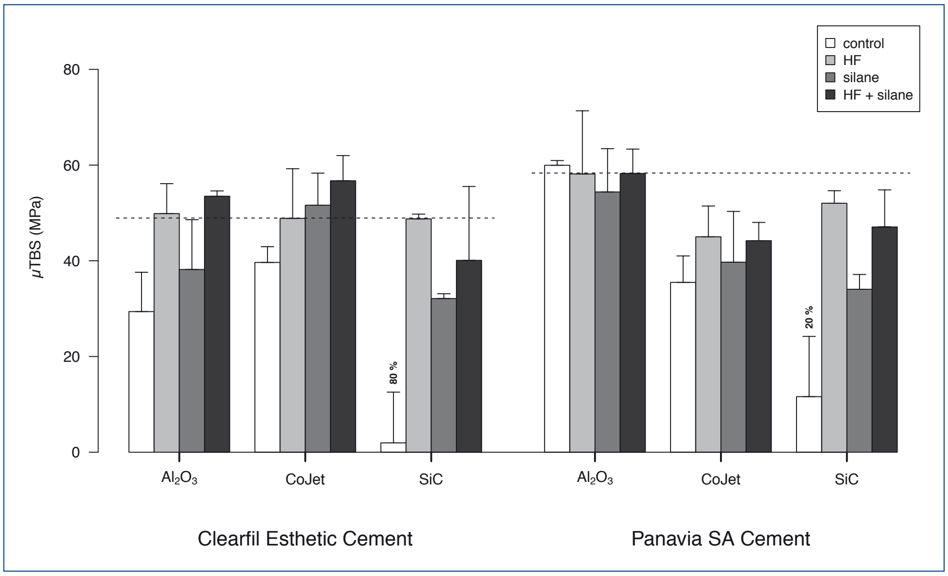

Fig 2F Bar graph of the mean μTBS (in MPa) for Lava Ultimate. Whiskers extend to the 95% confidence intervals as calculated from the respective linear mixed effects model. The dotted line represents the lower confidence limit of the best performing group; bars below this line are considered inferior to the best performing group. If pre-test failures occurred, the percentage of pre-test failures is given above the bar.

Table 3 Influence of the different parameters on the µTBS to the 6 CAD/CAM materials: p-values (linear mixed effects model)

p-values	Celtra Duo	IPS e. max CAD	IPS Empress CAD	Lava Ultimate	Vita Enamic	Vita Mark II
Cement	0.0012	0.0979	0.8731	<0.0001	0.4193	0.8787
MST	0.0117	0.0115	0.0844	<0.0001	0.2238	0.5674
S	0.0015	<0.0001	<0.0001	0.0015	<0.0001	<0.0001
HF	<0.0001	<0.0001	<0.0001	<0.0001	0.0001	<0.0001
Cement x MST	0.0035	0.0742	0.0427	0.0004	0.9218	0.0349
Cement x S	0.3908	0.0012	0.1260	0.0383	0.7944	<0.0001
Cement x HF	0.0021	0.9735	0.0379	0.0516	0.0888	0.9657
MST x S	0.7167	0.1574	0.1235	0.0922	0.0266	0.3294
MST x HF	0.0021	0.0934	0.9700	<0.0001	0.8990	0.3059
S x HF	0.0005	0.1553	<0.0001	<0.0001	0.0024	<0.0001

MST: mechanical surface treatment; S: silane; HF: HF acid etching.

Table 4 Effect sizes for different parameters from the linear mixed effects model in µTBS (MPa)

CAD/CAM material	Cement		Mechanical surface treatment			Chemical surface treatment			
	Clearfil Esthetic Cement	Panavia SAC	Al_2O_3	CoJet	SiC	No	S	HF	HF+S
Celtra Duo	27.9	16.8	23.0	22.3	21.7	0.4	9.2	41.5	38.5
IPS e.max CAD	29.4	18.7	23.2	29.0	20.2	1.7	19.8	27.1	50.3
IPS Empress CAD	26.1	24.9	29.5	23.9	23.1	1.0	41.3	24.2	35.9
Vita Mark II	25.2	23.1	22.5	23.7	26.5	1.3	38.5	25.3	32.5
Lava Ultimate	40.6	44.9	50.1	45.0	33.5	29.4	41.5	50.4	49.7
Vita Enamic	39.1	33.1	37.8	36.7	33.9	21.7	44.9	30.1	46.3

S: silane; HF: HF acid etching; HF+S: HF acid etching followed by silane application.

(Fig 3). For the ceramic materials (Celtra Duo, IPS e.max CAD, IPS Empress CAD), 100% adhesive failures were noticed after only mechanical surface treatment. For IPS e.max CAD and Lava Ultimate, cementation with Clearfil Esthetic Cement resulted in more adhesive failures, while more mixed failures were observed with Panavia SA Cement. Finally, the total percentage of adhesive failures was higher for IPS e.max CAD, Celtra Duo and Lava Ultimate.

DISCUSSION

The aim of the present study was to evaluate the bonding efficacy of two luting composites to six novel CAD/CAM materials. This study focused exclusively on a potentially weak link during adhesive luting procedures, ie, bonding of luting resin composite to the CAD/CAM material itself. The influence of different surface treatments on the bond strength to six CAD/CAM materials was evaluated. This has been tested in a few in vitro studies,[7,15,18,22,31] certainly for the more recently introduced zirconium-reinforced lithium silicate glass Celtra Duo,[5] the hybrid ceramic Vita Enamic, and the composite Lava Ultimate.[5,7,13,15] Celtra Duo lithium silicate glass ceramic contains 10 wt% highly dispersed zirconia. The zirconia is intended to serve as a thermodynamically favorable initiator for nucleation of crystals.[45] Vita Enamic is based on a polymer-infiltrated ceramic network material that consists of a dominant network (86 wt%) re-

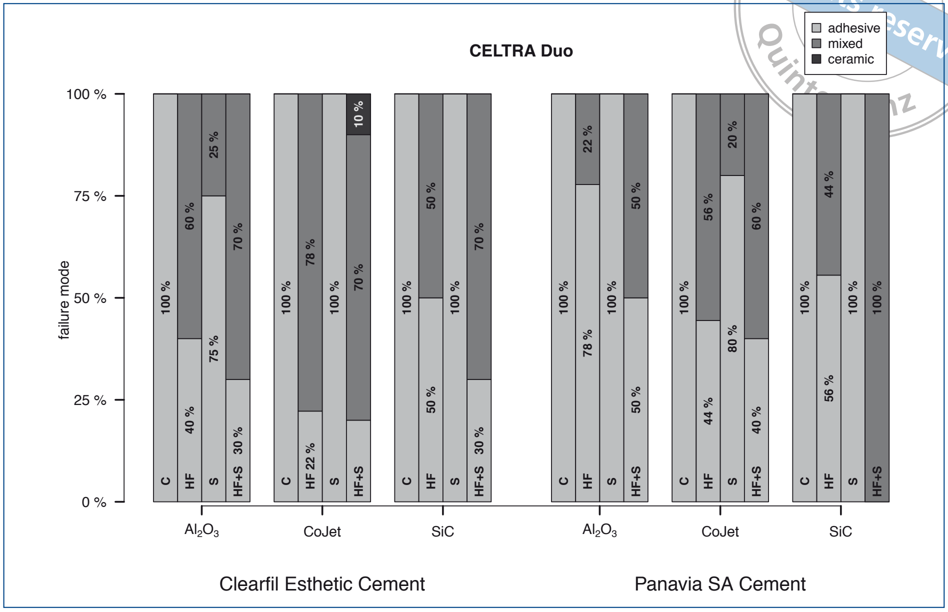

Fig 3A Proportions of failure modes by surface treatment, Celtra Duo.

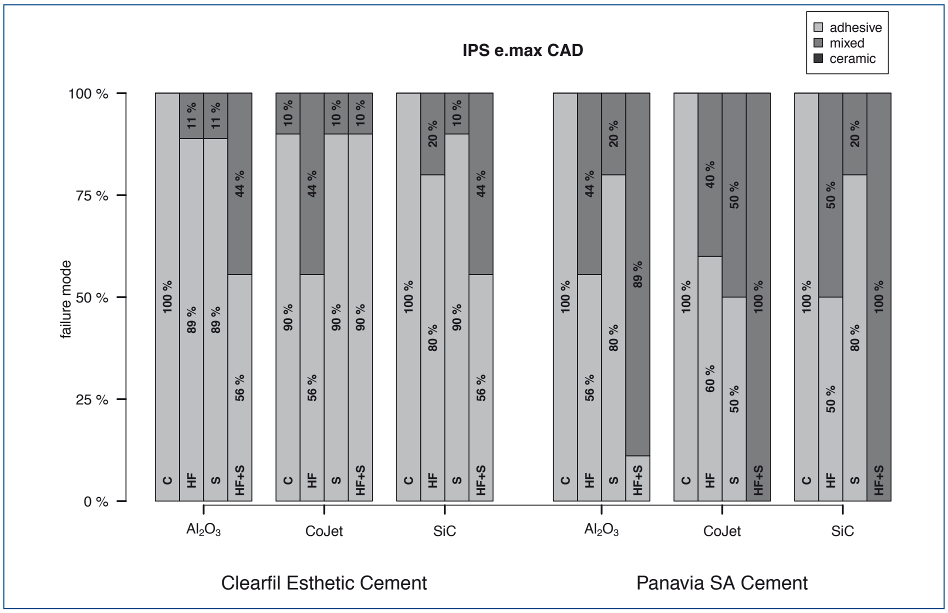

Fig 3B Proportions of failure modes by surface treatment, IPS e.max CAD.

inforced by an acrylic polymer network (14%), with both networks fully penetrating one another.[45] Lava Ultimate is a resin-based block nanocomposite, composed of 80 wt% zirconia/silica nanoceramic particles embedded in a highly cross-linked resin matrix (20 wt%).[8,45] As these new CAD/CAM materials are becoming increasingly used in daily practice, in vitro studies are necessary to determine the surface treatment that will result in the highest bond strength between the luting composite and the CAD/CAM restoration.

In this study, CAD/CAM restorative materials with the same surface treatment were bonded together instead of to dentin disks. The rationale was to avoid the weak link located in the tooth structure/luting system interface. Otherwise, failures might happen at other sites rather than at the restorative material surface, thus masking the effects of surface treatments.

In general, increasing surface roughness through mechanical surface treatment had less impact on µTBS than did chemical conditioning. Nevertheless, application of Al_2O_3 or CoJet did not reduce the µTBS. Sandblasting is generally anticipated to enhance bond strength by improving micromechanical interlocking, and increasing wettability and surface area.[13,37] However, sandblasting does not seem to be the best surface treatment for etchable ceramics, since it may cause microcracks in the ceramic surface, which may lead to premature failures. In addition, it influences internal and marginal adaptation.[7,13,37] Very low bond strengths (often close to zero) were measured for all

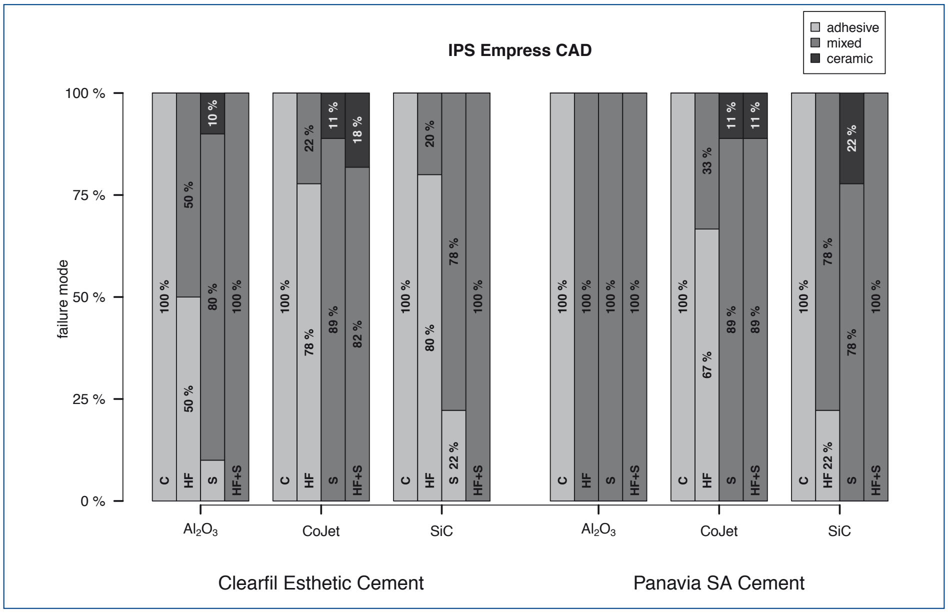

Fig 3C Proportions of failure modes by surface treatment, IPS Empress CAD.

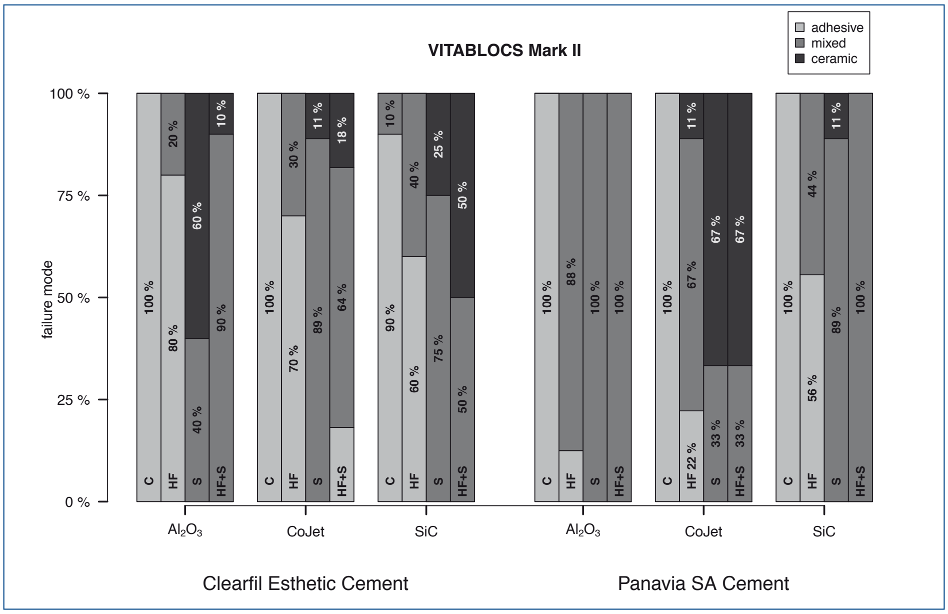

Fig 3D Proportions of failure modes by surface treatment, Vitablocs Mark II.

ceramic materials after only mechanical pretreatment. Moreover, most specimens showed pre-test failures (Fig 2). The positive effect of mechanical pretreatment on bond strength with Al_2O_3 or CoJet was highest for Lava Ultimate (Al_2O_3: 50.1 MPa; CoJet: 45 MPa; SiC: 33.5 MPa; $p < 0.0001$). This effect was less visible for Vita Enamic (SiC: 33.9 MPa; CoJet: 36.7 MPa; Al_2O_3: 37.8 MPa; $p = 0.223$), probably because of the significantly higher surface roughness after milling, as was found by Elsaka[13] (Tables 3 and 4). In the latter in vitro study, the surface topography of untreated Vita Enamic revealed two continuous interpenetrating networks: the polymer and the ceramic with micropores. The untreated Lava Ultimate showed a more homogeneous surface with tiny micropores.

For all CAD/CAM materials, HF, S, and the HF/S interaction had a significant beneficial influence on bond strength (Tables 3 and 4). Only for IPS e.max CAD was the interaction HF/S not significant. For each type of CAD/CAM block, the linear mixed models indicated the chemical surface treatment(s) that resulted in the highest bond strengths.

In all IPS e.max CAD groups, HF +S resulted in the highest bond strength, while for Celtra Duo, the preferred surface treatments were HF as well as HF+S. The application of S after HF acid etching did not have an additional effect on bond strength (38.51 MPa; $p = 0.0005$) (Tables 3 and 4). Failure analysis showed a slightly higher percentage of mixed failures in the HF+S than in the HF group (Figs 3A and 3B). Both manufacturers indicate HF + S as the optimal

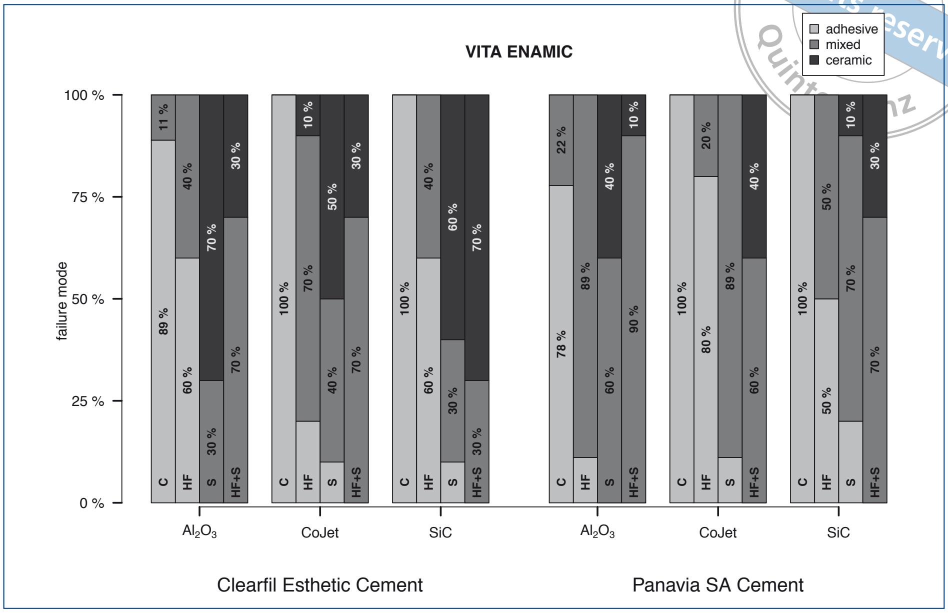

Fig 3E Proportions of failure modes by surface treatment, Vita Enamic.

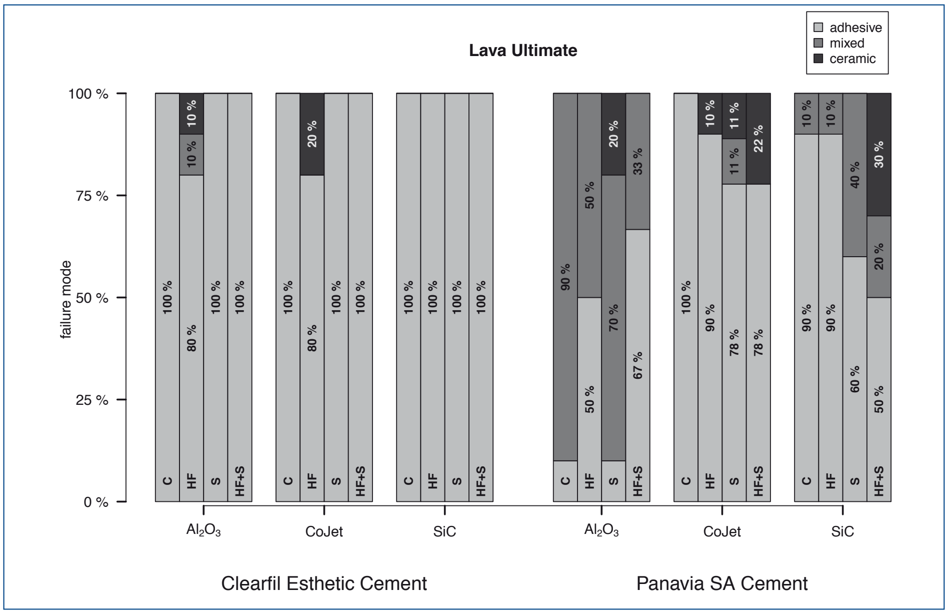

Fig 3F Proportions of failure modes by surface treatment, Lava Ultimate.

surface treatment before adhesive cementation. It must be emphasized that the HF acid etching time in this study was in accordance with the manufacturer's instructions. This must be taken into account because different concentrations of HF acid and different application times have an influence on bond strength to lithium disilicate glass.[18,39,43] Similarly, several in vitro studies confirmed that HF acid etching in combination with the use of silane is the best surface conditioning protocol for lithium disilicate glass ceramics [18,22,26,29,30,39] and the zirconium lithium silicate glass, Celtra Duo.[15] HF forms microporosities on the glass ceramic surface, increases the surface area, and enhances the establishment of mechanical interlocking with luting resin. Silane acts as a coupling agent in the glass ceramic-resin bond, which adsorbs onto the glass ceramic surface, thus facilitating chemical interaction.[29] The application of silane seems to be important for the durability of the bond, as was shown in several in vitro studies.[3,26,39]

For Vita Mark II and IPS Empress CAD, the highest bond strength values were recorded after application of S. In two out of six IPS Empress CAD groups and three out of six Vita Mark II groups, HF+S resulted in the highest bond strength (Figs 2C and 2D). In general, the bond strength with HF+S was lower than that with S; eg, for Vita Mark II, S yielded 38.5 MPa and HF+S 32.5 MPa, and for IPS Empress CAD, S yielded 41.3 MPa and HF+S: 35.9 MPa (Table 4). Failure analysis showed no adhesive failures in any HF+S group for either material (only 18% adhesive failures in the Vita Mark

II-Clearfil Esthetic Cement-CoJet group) (Figs 3C and 3D). HF+S is recorded as the preferred surface treatment in several in vitro studies[6,41] and is also indicated by both manufacturers. In the present study, the chemical bond promoted by the silane coupling agent was the mechanism largely responsible for the bond between luting composite and the glass ceramics Vita Mark II and IPS Empress CAD. The same observation was made in several in vitro studies,[3,9,10,14,33] while in other in vitro studies, HF acid etching contributed most to the bond strength between resin and feldspathic/leucite-reinforced ceramic.[17,32,35,38]

The optimal surface treatment for Vita Enamic in the present study was S and HF+S (Fig 2E). According to manufacturer's recommendations, Vita Enamic should be pretreated with HF acid etching and silane coupling agent. This was confirmed in three in vitro studies measuring bond strengths to Vita Enamic after aging.[7,13,15] In the study by Campos et al,[7] CoJet +S also resulted in the highest bond before aging. However, bond strength decreased significantly after aging. Etching with HF acid significantly increased the bond strength in the present study, but did not result in the highest bond strength. SEM evaluations of HF acid-etched Vita Enamic specimens by Elsaka[13] and Campos et al[7] showed a change in the surface morphology, with formation of numerous irregular and randomly distributed gaps and micropores. HF acid treatment appeared to partially dissolve the polymer and glassy phases of Vita Enamic, which possibly served for micromechanical retention of the bonding resin. Campos et al[7] recorded a higher contact angle after HF acid etching of Vita Enamic compared to Vita Mark II. A possible explanation for this phenomenon is that the surface becomes more hydrophilic due to the dissolution of the glass matrix. Silane application can additionally increase the surface wetting. Silane application with or without mechanical surface treatment also resulted in the highest bond strength (Fig 2E). The rather rough surface of the untreated Vita Enamic block[13] in combination with the high bonding capacity of Monobond Plus[2,31] can explain this observation. Regarding failure analysis, no adhesive failures were recorded in the HF+S group for either luting cement. The S group showed some adhesive failures (10% to 20%) in four out of six groups (Fig 3E). Therefore, HF+S and S can be considered as the preferred surface treatments for Vita Enamic.

For Lava Ultimate, all mechanical and chemical surface treatments resulted in high bond strengths (>29 MPa). Similarly, in the study by Elsaka,[13] all surface treatments (sandblasting, sandblasting + silane, HF, HF+S) showed comparable enhancement of bond strength values vs those of the control group. A self-adhesive luting composite, Bifix SE (VOCO; Cuxhaven Germany), was used for the cementation procedure. In the present study, different results were seen for the two luting cements (Fig 2F). For Panavia SA Cement, the highest bond strengths were obtained after Al_2O_3 pretreatment with or without subsequent chemical surface treatment. The manufacturer's recommended surface treatment consists of sandblasting (Al_2O_3 or CoJet), followed by application of silane or a universal bonding agent. In the present study, this surface treatment resulted in the highest bond strengths only for Panavia SA Cement. For Clearfil Esthetic Cement, HF and HF+S resulted in the highest bond strength in all groups. In general, HF acid etching had a significant positive effect on bond strength (50.41 MPa; $p < 0.0001$). A similar result was noticed by Elsaka,[13] although SEM characterization showed that Lava Ultimate specimens were slightly resistant to HF treatment. Tiny micropores and pits appeared on the Lava Ultimate surface without extensive dissolution of the glassy phase. In the study by Frankenberger et al,[15] HF has a detrimental effect on bond strength.

The type of surface treatment at which the highest bond strength was observed was quite similar for both luting composites. For 5 out of 6 CAD/CAM materials, Panavia SA Cement showed lower bond strengths than did Clearfil Esthetic Cement (Fig 2). However, this was only statistically significant for Celtra Duo ($p = 0.0012$). A possible explanation is offered by the differences in physicomechanical properties, wettability, and chemical composition between the two luting composites.[41] The filler load, compressive strength, and flexural strength are slightly higher for Clearfil Esthetic Cement (filler 70 wt%, 49 vol%; compressive strength 290 MPa, flexural strength 110 MPa; flexural modulus 6.5 GPa) than for Panavia SA Cement (filler 45 vol%; flexural strength: 98 MPa) as stated by the manufacturer. Several in vitro studies also found a lower bond strength of self-adhesive cements to composite or ceramic materials compared to a conventional luting composite.[15,22,37] Lava Ultimate was the only material for which the bond strength values for Panavia SA Cement were significantly higher than for Clearfil Esthetic Cement ($p < 0.0001$). This observation may be explained by differences in surface topography, surface energy of the CAD/CAM material, surface tension of the luting cement, and other factors.

Bond strengths between different CAD/CAM materials were not compared in the present study, mainly because the very different material properties (mainly e-modulus) affect the µTBS values[40] and thus invalidate comparisons between different CAD/CAM block types. For clinical use, the choice of CAD/CAM block is also mostly based on other parameters, such as strength, esthetics, and marginal accuracy. The purpose of this study was not to compare bond strengths between CAD/CAM materials but to identify the necessary mechanical and chemical pretreatments for each block type. Apart from a change in µTBS value, the failure mode may also change with block type. For the CAD/CAM materials with a higher flexural strength (IPS e.max CAD: 360 MPa; Celtra Duo: 420 MPa; Lava Ultimate: 200 MPa[45]), more adhesive failures were recorded. This may be due to some stress concentration present at the boundary of high (ceramic) and low e-modulus (composite cement) materials during tensile loading,[27] resulting in more failures at this interface. An increase in interfacial failures with IPS e.max CAD was also observed in the in vitro study by Sunfeld Neto et al.[39] Regarding failures analysis, for each CAD/CAM material, a correlation was noticed between bond strength and failure type (Fig 3). More adhesive failures were seen with lower bond strengths. For all materials (except Vita Enamic), 100% adhesive failures were seen after only mechanical pretreatment. These groups also showed many pre-test failures (Fig 2).

Finally, it must be emphasized that in the present study immediate bond strengths were measured. Only a few studies evaluated bond strength after aging. They showed that for all materials, bond strength decreases with time.[6,7,13,15,16,26,31,37] In addition, the positive influence of silane on the durability of bond strength was visible after aging.[12,26,33] More in vitro studies are needed to evaluate the influence of aging on bond strength to these novel CAD/CAM materials after different surface treatments. In a following in vitro study with a similar study design, the influence of aging (water storage) on the bond strength will be investigated.

CONCLUSION

The bond strength to novel CAD/CAM materials is influenced by surface treatment and luting composite. Each CAD/CAM material/luting composite must be studied individually to define an optimal bonding protocol. In addition, the effect of aging needs to be examined in depth.

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Clinical relevance: The bond strength to novel CAD/CAM materials is influenced by surface treatment and luting composite. Each CAD/CAM material/luting composite combination needs to be studied individually to define an optimal bonding protocol.