Stephanie Pfeffer, Silke Jacker-Guhr, Werner Geurtsen, Tobias Alexander Pfeffer, Anne-Katrin Lührs

Microtensile bond strength of luting cements to a 3D printable composite – an in vitro study

Introduction: The aim of this in vitro study was to investigate the adhesion of 3 different luting cements (resin-modified glass ionomer cement, self-adhesive resin cement, and composite cement) to a 3D printable composite material by testing the microtensile bond strength (μTBS).

Material and Methods: For this study, 72 square-shaped blocks (16 x 16 x 4 mm) of composite (K&B-EXP, BEGO Bremer Goldschlägerei Wilh. Herbst GmbH & Co. KG, Bremen, Germany) were printed and divided into 18 groups. Each group corresponded to a luting cement, a pretreatment method and an aging procedure. Cementation involved the luting process of 2 blocks with the respective cement resulting in so-called "sandwich" blocks. In addition to the type of cement used, the blocks differed in regard to the type of pretreatment: either blast polishing with sodium bicarbonate glass (50 μm) alone, or in combination with sandblasting with aluminum oxide (50 μm). For each group, the sandwich blocks were sectioned into microsticks, which were then subjected to microtensile testing. The sticks were tested initially (24 h water storage), after aging (10,000 cycles of thermocycling [5/55 °C] or after 6 months of long-term water storage). All sticks were examined using light microscopy to determine their fracture pattern. The statistical analysis of the data was carried out using ANOVA, the Tukey HSD test, and the Chi-square test.

Results: The one-way ANOVA showed significant differences between the groups ($p \leq 0.05$). The highest bond strength was measured for the composite cement in combination with aluminum oxide pretreatment. The resin-modified glass ionomer cement showed the significantly lowest bond strength regardless of the pretreatment. When no additional sandblasting with aluminum oxide was performed, the bond strength of the self-adhesive resin and composite cements were comparable.

Conclusion: The highest bond strength is achieved using either a self-adhesive resin cement or composite cement. Sandblasting with aluminum oxide leads to a significant increase in the adhesion values for the composite cement.

Keywords: 3D-Printing; CAD/CAM; microtensile bond strength test; adhesion; sandblasting; composite

Department of Conservative Dentistry, Periodontology and Preventive Dentistry, OE 7740, Hannover Medical School: Stephanie Pfeffer, Dr. Silke Jacker-Guhr, Prof. Dr. Werner Geurtsen, Tobias Alexander Pfeffer, PD Dr. Anne-Katrin Lührs
Translation from German: Cristian Miron
Citation: Pfeffer S, Jacker-Guhr S, Geurtsen W, Pfeffer TA, Lührs AK: Microtensile bond strength of luting cements to a 3D printable composite – an in vitro study. Dtsch Zahnärztl Z Int 2020; 2: 229–239
Peer-reviewed article: submitted: 14.02.2020, revised version accepted: 09.04.2020
DOI.org/10.3238/dzz-int.2020.0229–0239

1. Introduction

In the age of digitalization, computer-aided manufacturing processes have become well-established in restorative dentistry [5, 22]. At the beginning, when the production of dental restorations became digitally supported, ceramic was the only material option for a CAD/CAM restoration [10, 17]. CAD stands for computer-aided design and CAM for computer-aided manufacturing [30]. Nowadays, besides various dental ceramics, temporary and permanent composites can also be processed using CAD/CAM technology [10, 26]. Currently, new additive techniques, such as 3D-Printing, present alternatives to the conventional manufacturing process of digitally designed restorations, which is based upon subtractive techniques [2]. The importance of dental 3D-printing, also known as additive manufacturing, has increased over time [5]. Additive technology enables the construction of an object regardless of its morphological complexity or size [2, 28]. Different technical procedures are used in 3D-printing and a distinction is made based on the type of material to be printed, or alternatively, according to the method used for manufacturing, i.e. the actual additive process. In this case, a differentiation is made between build-up by polymerization, bonding and fusing [24, 25].

When a construction is made by polymerization, a distinction can be made between stereolithography (SLA) and digital light processing (DLP) [25]. In the SLA process, a laser beam triggers a photochemical reaction in the liquid printing material, which then causes it to harden according to the CAD template. This is repeated layer by layer until the construction is complete [2, 25]. The DLP technique is based on a variant of stereolithography. In this case, the liquid polymers are also solidified by means of a digital light projection source, but high-performance LEDs are used for this purpose. Complete layers can be projected and simultaneously polymerized onto the liquid printing material [2, 25].

There are now a wide variety of applications for 3D-printing in dentistry, including printing of templates, models, splints, retainers, brackets, denture frameworks, single-tooth restorations and temporary crowns and bridges [25, 30, 31].

An important factor for a clinical sufficient long-term stability is the adhesion of the luting cement to the indirect restoration and tooth. Previously, the prerequisite for indirect restorations was a retentive preparation method, which also relied on a mechanical interlocking of the cement (e.g. zinc phosphate cement) with the rough surface of the prepared tooth [19]. Glass ionomer cements have a low adhesive potential, as they form weak chemical bonds with the hydroxyapatite of enamel and dentin via ionic and hydrogen bonds [18]. The development of adhesive systems, composite cements, surface treatments for various ceramic and composite-based materials as well as silanization processes have broadened the application range of indirect restorations (e.g. ceramic veneers; ceramic inlays, onlays or partial crowns; indirect composite restorations) and made it possible to adhesively bond the restoration to the tooth [8, 23].

The adhesion between different luting cements and the tooth structure has been investigated extensively, but until now, there is hardly any scientific data related to their adhesion to novel 3D-printable composites intended for indirect restorations.

Therefore, the aim of this in vitro study was to investigate the microtensile bond strength of 3 luting cements to a 3D printable composite material in relation to various surface treatments and aging processes.

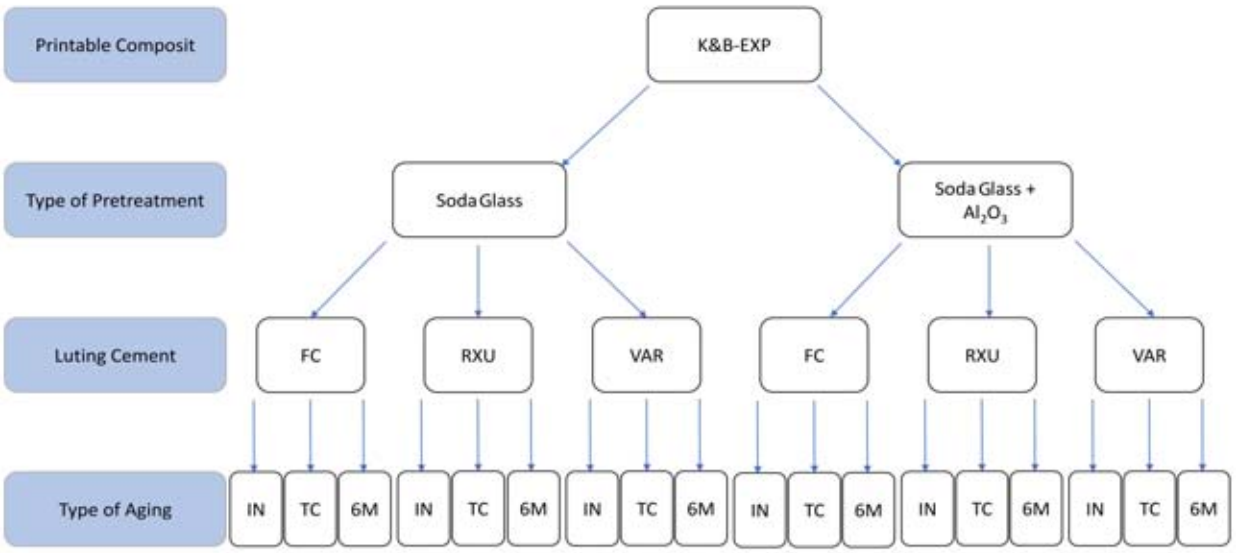

Figure 1 Illustration of the experimental groups. FC = GC FujiCEM 2, resin-modified glass ionomer cement; RXU = RelyX Unicem 2, self-adhesive composite cement; VAR = Variolink Esthetic DC, composite cement; IN = 24 h water storage at 37 °C; TC: 10,000 cycles of thermocycling (5/55 °C); 6M: 6-month water storage at 37 °C.

Material	Description and Composition	Color	Manu-facturer	Application	Batch / LOT-Nr.
K&B-EXP	Light-curing, flowable resin-based on methacrylic acid esters: ethoxy-lated bisphenol A-dimethacrylate, silanized dental glass, initiators, inhibitors	A2 Dentin	BEGO Bremer Goldschlägerei Wilh. Herbst GmbH & Co. KG, Bremen, Germany	Post-processing after completion of printing process: 1. cleaning in an unheated ultrasonic bath a. 3 min in a reusable ethanol solution (96 %) b. 2 min in a fresh ethanol solution (96 %) 2. drying using compressed air 3. light exposure using HiLite Power (Kulzer GmbH, Hanau, Germany) 4. blast polishing with Perlablast micro (see below) 5. cleaning using compressed air	K&B_2018–110
Perla-blast® micro	Lead-free soda glass (grain size 50 µm)	n.a.	BEGO Bremer Goldschlägerei Wilh. Herbst GmbH & Co. KG, Bremen, Germany	Blast polishing the sample's surface from a distance of 6 cm for 8 sec at 1.5 bar	A54474
Aluminum Oxide	50 µm aluminum oxide (Al_2O_3)	n.a.	Ronvig Dental Mfg. A/S, Daugård, Denmark	Sandblasting the sample's surface carefully from a distance of 6 cm for 8 sec at 1.5 bar	1906
GC Fu-jiCEM® 2	Radiopaque resin-modified glass ionomer luting cement: 2-Hydroxyethyl methacrylate2, 2'-ethylenedioxy-diethyldimetha-crylate 7,7,9 (or 7,9,9)- Trimethyl-4,13-dioxo-3,14-dioxa-5,12-diaza-hexadecane-1,16-diylbismethacry-late	Light-yellow	GC Europe N.V., Leuven, Belgium	Uniform wetting of the sample's surface with the cement. Pro-cessing time after the start of mixing: 2'15 min at 23 °C. Start of cutting procedure using saw after 4'30 min	1805172
RelyX™ Unicem 2 Automix	Dual-curing, self-adhesive com-posite luting cement: Glass powder, surface with 2-propenoic acid, 2 methyl-. 3-(trimethoxysilyl)propyl ester, bisphenol A bis(3-methacryloyloxy-propyl)ether substituted dimetha-crylate, sodium toluene-4-sulphi-nate, 1,12-dodecanediylbismetha-crylate, 1-benzyl-5-phenyl-barbic acid, calcium salt, silicic acid, me-thacrylic aliphatic amine, calcium dihydroxide, 2-[(2-hydroxye-thyl)(3-ethoxypropyl)amino]ethyl methacrylate, 2,6-di-tert-butyl-p-cresol, titanium dioxide	translu-cent	3M Deutsch-land GmbH, Neuss, Germany	Uniform wetting of the sample's surface with the cement. Curing performed based on curing protocol	4407807
Mono-bond® Plus	Universalprimer: Alcoholic solution of silane methacrylate, phosphoric acid methacrylate and sulfide me-thacrylate	n.a.	Ivoclar Viva-dent GmbH, Ellwangen, Germany	Application of Monobond Plus using a microbrush, reaction time of 60 sec, then blowing with compressed air	X34950
Variolink® Esthetic DC	Adhesive bonding system: Ure-thane dimethacrylate, methacrylate monomers. Ytterbium trifluoride, spheroidal mixed oxide, initiators (including ivocerine), stabilizers, pigments.	neutral	Ivoclar Viva-dent GmbH, Ellwangen, Germany	Uniform wetting of the sample's surface with the cement. Curing performed based on curing protocol	X29747

Table 1 Materials, manufacturer and application

The null hypotheses which were set forth are:

1. The bond strength of various cements belonging to different material classes to the 3D printable composite do not differ.
2. The type of pretreatment applied on the adhesive surface does not influence the bond strength.
3. The aging processes do not influence the bond strength.

2. Materials and Methods

The adhesion of 3 different luting cements to a 3D-printable material (K&B-EXP, BEGO Bremer Goldschlägerei Wilh. Herbst GmbH & Co. KG, Bremen, Germany) was investigated after 2 different surface pretreatments by means of microtensile bond strength testing (μTBS = microtensile bond strength). The following luting cements were used:

- resin-modified glass ionomer cement (GC FujiCEM 2, GC Europe N.V., Leuven, Belgium) (GIZ)
- self-adhesive composite cement (RelyX Unicem 2, 3M Deutschland GmbH, Neuss, Germany)
- composite cement in combination with a silane (Variolink Esthetic DC/Monobond Plus, Ivoclar Vivadent GmbH, Ellwangen, Germany)

Two types of surface pretreatments were examined: blast polishing with a polishing agent (sodium bicarbonate glass) vs. blast polishing with sodium bicarbonate glass and additional sandblasting with aluminum oxide. The pretreatment was performed according to a standardized test protocol and the manufacturer's specifications.

Table 1 shows the materials which were used in this study and their application.

K&B-EXP is a light-curing, flowable resin based on methacrylic acid esters, which can be processed using DLP-based printers. The application range includes single crowns, inlays, onlays and veneers. The flexural strength is specified as ≥ 100 MPa [6]. The material was processed and treated according to the manufacturer's instructions. A preliminary version of the instructions for use was provided by BEGO Bremer Goldschlägerei Wilh. Herbst GmbH & Co. KG. In order to test the microtensile bond strength of the various types of cements to this Bis-DMA-based printable composite, square blocks with a thickness of 4 mm and an edge length of 16 mm were printed (3D-Printer Varseo, BEGO Bremer Goldschlägerei Wilh. Herbst GmbH & Co. KG, Bremen, Germany). After the printing process was complete, the specimens were cleaned in 2 steps using a 96 % ethanol solution in an unheated ultrasonic bath (3 minutes in reusable solution, 2 minutes in fresh solution). The test specimens were dried using compressed air. Finally, they were exposed to 3 cycles of light-curing for 90 seconds according to the manufacturer's instructions using the HiLite Power high-performance light-curing device (Kulzer GmbH, Hanau, Germany).

Four test specimens were prepared for each group (luting cement/surface treatment/aging). The surface of all the samples was carefully blast polished from a distance of 6 cm for 8 seconds at 1.5 bar with sodium bicarbonate glass (Perlablast micro 50 μm) based on the manufacturer's recommendations. Each cement type was examined once with and without additional surface pretreatment. For the additional pre-treatment, the samples were sandblasted with aluminum oxide 50 μm (same parameters as with Perlablast). Subsequently, the surface of the samples was cleaned with compressed air to remove any abrasive material residues. Immediately after blasting, the samples were further processed. Each experimental group and its respective coding are represented in Table 2 and Figure 1.

After the application of each luting cement, 2 test specimens, which were pretreated in the same manner, were luted together with the corresponding cement under a standardized load of 1 kg to form a so-called sandwich block [14]. For groups 1–6, all samples were loaded for 4'30 minutes before starting the sectioning of the samples. For groups 7 to 18, light-curing started 10 seconds after applying the standardized load.

All sandwich blocks were light-cured with a Bluephase G2 LED light-curing unit (Ivoclar Vivadent, Ellwangen, Germany) according to the following light-curing protocol:

- side: 2 x 20 seconds per surface, overlapping (total 160 seconds)
- upper and lower surface: each surface for 4 x 20 seconds, overlapping (total 160 seconds)

This results in a total light-curing time of 320 seconds for each sandwich block.

The light output of the lamp (required to be ≥ 1000 mW/cm^2) was checked and recorded before each curing cycle using a measuring device (Bluephase Meter, Ivoclar Vivadent, Ellwangen, Germany). The upper side of the sandwich blocks was marked with a waterproof pencil after light-curing was complete. This procedure ensured that all sticks were later glued to the brass holders of the testing machine in the same direction.

The sticks were then cut, using a computer-controlled precision saw (IsoMet High Speed Precision Saw, Buehler, ITW Test & Measurement GmbH European Headquarters, Esslingen am Neckar, Germany). For each sandwich block, 7 cuts in x- and 5 cuts in y-direction were made in order to obtain 24 sticks per block (total number per group: 2 sandwich blocks/48 sticks). Depending on the type of aging, the sticks were tested either initially (24 h water storage at 37 °C, n = 48), after 10,000 cycles thermocycling (5/55 °C, dwell time 30 seconds, transfer time 10 seconds; n = 48), or after 6-month water storage at 37 °C (n = 48). Before microtensile testing was performed, each stick was measured using a digital caliper (depth x width in mm) in order to determine the bonded area for each stick. The adhesive area per stick was approximately 1 mm^2, a deviation of not more than 0.05 mm in depth and width was accepted, as specified by Armstrong et al. [4]. All sticks were glued to brass holders attached to a microtensile testing device (MTD-500+, SD Mechatronik GmbH, Feldkirchen-Westerham, Germany) without pressure using cyanoacrylate glue (Roxolid Aktiv-X Liquid and Roxolid Aktiv-X Spray, Meffert AG Farbwerke, Bad Kreuznach, Germany). The specimens were then loaded until fracture and the maximum force, which occurred, was recorded (crosshead speed: 1 mm/min). Sticks which fractured due to

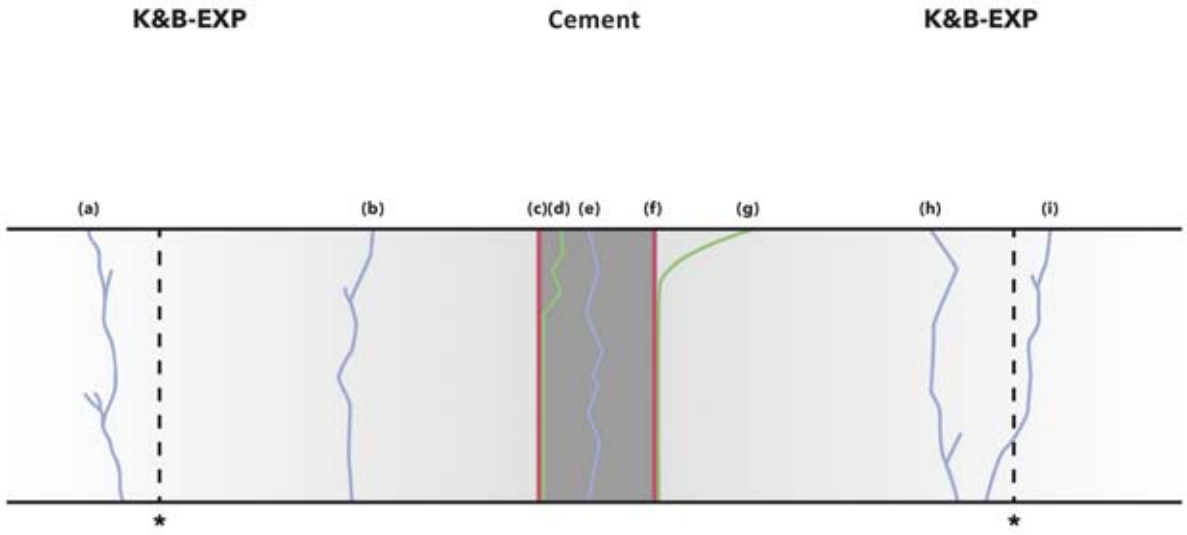

Figure 2 Possible fracture patterns during the μTBS test and their validity for statistical evaluation. a, b, h, i: cohesive fracture in composite resin; e: cohesive fracture in cement; c, f: adhesive fracture; d, g: mixed fracture (d = interface and cement; g = interface and composite resin); *fractures ≥ 2 mm distance from the interface were not included in the statistical analyses.

handling mistakes during attachment to the brass holders were excluded from the statistical analysis. Sticks which fractured during cutting or thermocycling (TC) were included in the statistical analyses as zero bonds.

After microtensile testing, all specimens were examined using light microscopy for determining their fracture patterns (magnification 50x, Stemi SV6, ZEISS, Jena, Germany). A distinction was made between adhesive, cohesive or mixed fracture patterns.

The classification of fractures was performed as described by Armstrong et al. [4]. Fractures which occurred at a distance of ≥ 2 mm from the interface (see fracture patterns a, i, Figure 2) were excluded and not statistically analyzed. For all other samples, a distinction was made between the fracture patterns as shown in Figure 2.

The statistical analysis of the data was performed with SPSS (IBM SPSS Statistics Version 25, New York, USA). The normal distribution of the values was checked using the Kolmogorov-Smirnov test. The results were then analyzed using one-way ANOVA and the Tukey HSD test, while the fracture pattern was analyzed using the Chi-square test.

3. Results

According to the Kolmogorov-Smirnov test, the data was normally distributed. The one-way-ANOVA showed significant differences between the experimental groups ($p \leq 0.05$).

3.1 Influence of the cement type on μTBS

Initially, the significantly lowest μTBS could be detected for the glass ionomer cement without aluminum oxide pretreatment (Table 3, $p < 0.001$). The bond strength of the self-adhesive resin cement and the composite cement was significantly higher, but did not differ from the other groups.

After TC, similar results were present as the bond stength of the glass ionomer cement was significantly lower ($p < 0.001$) when compared to the self-adhesive resin cement and composite cement.

Also, after 6-month water storage, the lowest bond strength was measured for the glass ionomer cement, which was significantly different when compared the self-adhesive resin cement and the composite cement. All results are shown in Table 3 and Figure 3.

3.2 Influence of pretreatment on μTBS

In the case of the glass ionomer cement, pretreatment of the surface with aluminum oxide initially led to a significant increase of the bond strength ($p < 0.001$). After TC and 6-month water storage, this difference was no longer detectable (Figure 3).

For the self-adhesive resin cement, sandblasting did not influence the bond strength initially and after TC. Only after 6-month water storage, a significantly higher bond strength was measured for the groups which were additionally sandblasted with aluminum oxide as compared to those treated just with sodium bicarbonate glass ($p < 0.001$).

Initially, the composite cement showed a significant increase in adhesion when the surface was sandblasted with aluminum oxide ($p < 0.001$, Table 3 and Figure 3). This effect was also detectable after TC and after water storage.

3.3 Influence of aging on μTBS

For the glass ionomer cement, a significant decrease in bond strength was observed after water storage after pretreatment with sodium bicarbonate glass as well as after sandblasting with aluminum oxide (Table 3 and Figure 3, $p < 0.001$).

Long-term water storage also significantly influenced the bond strength of the self-adhesive resin cement ($p < 0.001$). Pretreatment with sodium bicarbonate glass led to a de-

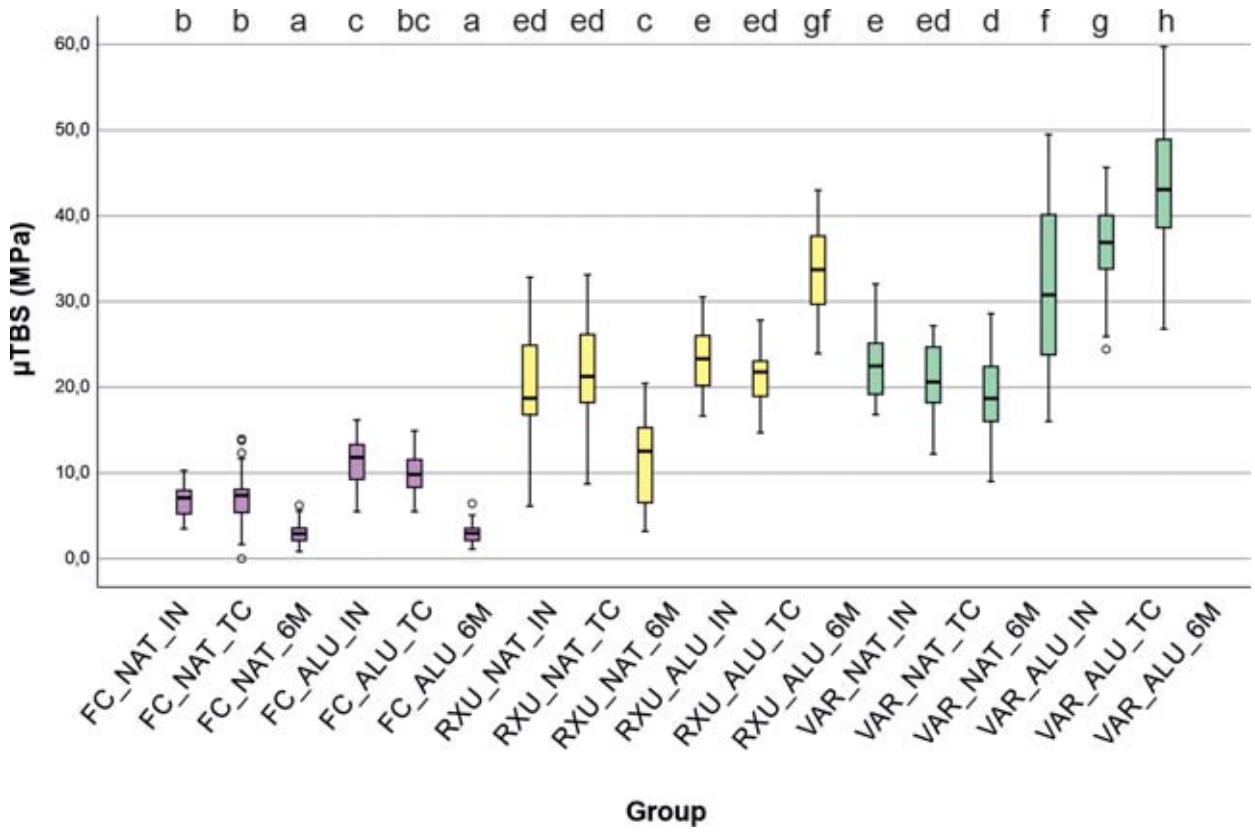

Figure 3 Results of the microtensile test in MPa, horizontal line in the box plot represents the median value, outliers are shown in a circle, indication of significance levels (a–h)

crease ($p < 0.001$), additional sandblasting with aluminum oxide to an increase of bond strength ($p < 0.001$). TC had no significant influence on the bond strength.

In the case of the composite cement, pretreatment with sodium bicarbonate glass coupled led to a reduction in adhesion after 6-month water storage ($p = 0.010$), while aluminum oxide pretreatment resulted in a significant increase in bond strength ($p < 0.001$). After TC, the samples, which were pretreated with sodium bicarbonate glass, showed no significant differences. For sandblasting with aluminum oxide, TC led to an increase in bond strength. However, the values were lower when compared to those after 6-month water storage (Table 3 and Figure 3).

3.4 Assessment of the levels of significance

The lowest significance levels (a–c) were found for all groups of the resin-modified glass ionomer cement, as well as for the self-adhesive resin cement after pretreatment with sodium-bicarbonate glass and long-term water storage. The composite cement and the self-adhesive resin cement with aluminum oxide pretreatment after 6 months water storage had the highest significance levels (f–h, Figure 3).

3.5 Fracture analysis

The Chi-square test showed significant differences between the test groups ($p < 0.001$). Regarding the overall distribution of the fracture patterns, adhesive fractures (66.79 %) predominate, followed by mixed fractures (23.49 %) and cohesive fractures in the printable composite (9.13 %). Cohesive fractures in the luting cement accounted for the smallest part of the overall distribution (0.59 %).

When evaluating the groups separately, the glass ionomer groups displayed only adhesive fractures or mixed fractures. Adhesive fractures predominated initially and after TC for both types of pretreatment (FC_NAT_IN: 79 %, FC_NAT_TC: 87 %, FC_ALU_IN: 65 %, FC_ALU_TC: 75 %). The fracture patterns of these groups were not significantly different. After 6 months of water storage, mixed fractures occurred in both pretreatment groups (up to 100 %). The fracture patterns of these groups were significantly different when compared to the initial values and the patterns after TC ($p < 0.001$).

In the case of the self-adhesive resin cement, adhesive fractures predominated in each group (RXU_NAT_IN: 94 %, RXU_NAT_TC: 98 %, RXU_NAT_6M: 100 %, RXU_ALU_IN: 75 %, RXU_ALU_TC: 94 %, RXU_ALU_6M: 58 %). Initially, there were no differences regarding the fracture patterns in the groups pretreated with sodium bicarbonate glass. After TC or water storage, the fracture patterns differed significantly from the initial fracture patterns in the aluminum oxide pretreated groups ($p = 0.013/p < 0.001$). Cohesive fractures in the printed composite

Cement	Pretreatment	Silane	Aging	Code	Group
GC FujiCEM® 2	Soda glass	-	Initial[1]	FC_NAT_IN	1
			Thermocycling[2]	FC_NAT_TC	2
			6 Mon. 37 °C H_2O [3]	FC_NAT_6M	3
	Soda glass + Al_2O_3	-	Initial[1]	FC_ALU_IN	4
			Thermocycling[2]	FC_ALU_TC	5
			6 Mon. 37 °C H_2O [3]	FC_ALU_6M	6
RelyX™ Unicem 2 Automix	Soda glass	-	Initial[1]	RXU_NAT_IN	7
			Thermocycling[2]	RXU_NAT_TC	8
			6 Mon. 37 °C H_2O [3]	RXU_NAT_6M	9
	Soda glass + Al_2O_3	-	Initial[1]	RXU_ALU_IN	10
			Thermocycling[2]	RXU_ALU_TC	11
			6 Mon. 37 °C H_2O [3]	RXU_ALU_6M	12
Variolink® Esthetic DC	Soda glass	Monobond® Plus	Initial[1]	VAR_NAT_IN	13
			Thermocycling[2]	VAR_NAT_TC	14
			6 Mon. 37 °C H_2O [3]	VAR_NAT_6M	15
	Soda glass + Al_2O_3	Monobond® Plus	Initial[1]	VAR_ALU_IN	16
			Thermocycling[2]	VAR_ALU_TC	17
			6 Mon. 37 °C H_2O [3]	VAR_ALU_6M	18

Table 2 Coding of the experimental groups. 1) Initial, 24 h water storage at 37 °C. 2) Thermocycling, 10,000 cycles, 5/55 °C. 3) Water storage for 6 months at 37 °C

occurred initially for both types of pretreatments and in the groups pretreated with aluminum oxide also after aging.

Similarly, for the composite cement, the majority of fractures were adhesive (VAR_NAT_IN: 67 %, VAR_NAT_TC: 55 %, VAR_NAT_6M: 74 %, VAR_ALU_IN: 60 %, VAR_ALU_TC: 67 %, VAR_ALU_6M: 55 %). In the case of pretreatment with sodium bicarbonate glass, the initial fracture patterns differed significantly from the fracture patterns after aging ($p < 0.001$). The aluminum oxide pretreated groups showed no differences in fracture modes. Cohesive fractures in the printed composite and mixed fractures occurred to a varying amount in each group (Table 3).

4. Discussion

The first two null hypotheses must be rejected based on the existing results because

1. the adhesion values of the three cements to the 3D-printable material differ significantly and
2. the type of pretreatment significantly influences the microtensile bond strength.

The third null hypothesis is only partly rejected because TC significantly influenced the bond strength in one group with aluminum oxide pretreatment (VAR_ALU_TC). The second aging process (6-month water storage) significantly changed the adhesion values in each group. In two groups with aluminum oxide pretreatment (RXU_ALU_6M and VAR_ALU_6M), water storage resulted in a significant increase in bond strength, but in all other groups it led to a significant decrease (see Figure 3 and Table 3). A possible explanation for the increased adhesion may be related to the storage of the samples at 37 °C; this may increase the degree of conversion by cross-linking of the re-

maining monomers, and consequently, outweigh the effect of the aging process. Additionally, the longer storage time could result in unbound monomers being able to further react and complete the polymerization process [11].

4.1 Discussion of methods

In this study, the adhesion between a printable composite and various cements was tested by bonding 2 blocks of this material together for each cement in order to form sandwich blocks [3, 14, 22]. This procedure can be regarded as a first "preliminary investigation" which examined the adhesion of various cements without further influencing factors such as a high C-factor, more complicated cavity geometries or additional bonding surfaces, e.g. dentin, etc..

Pretreatment of the printable composite with sodium-bicarbonate glass was recommended by the manufacturer (grain size 50 µm, 1.5 bar, distance to the surface 5–10 cm, duration 5–10 seconds). In order to standardize the testing procedure, a constant distance of 6 cm and a duration of 8 seconds was used, and blasting was performed after light-curing was completed. The whole procedure based on the manufacturer's instructions for the experimental printable composite. In this study, an aluminum oxide with a grain size of 50 µm was used for the additional surface pretreatment, similar to studies performed by Ali et al., Tekçe et al., Kassotakis et al. and Sadighpour et al. [3, 29, 13, 26]. The experimental procedure was identical to the one applied for the sodium-bicarbonate glass groups. This additional step was used to roughen the surface in order to create a microretentive surface pattern [7, 27, 29]. For both sodium-bicarbonate glass and aluminum oxide, the same grain size (50 µm) was used. However, in some groups with additional aluminum oxide treatment, an improvement of the microtensile bond strength resulted. This could be explained by the fact that aluminum oxide is harder than sodium-bicarbonate glass (9 Mohs [16] vs. 6–7 Mohs [6]), and therefore, it causes a more pronounced surface change. For the composite surfaces pretreated in this manner, the pretreatment appears to have a positive effect on the wetting properties of the silane agent, and consequently on adhesion, because these groups exhibit significantly higher adhesion values. For the far more viscous resin-modified glass ionomer cement and self-adhesive cement, this effect was less pronounced. Only in cases where the samples were aged by water storage for 6 months, significant differences existed due to sandblasting.

After sandblasting, the surface was thoroughly cleaned with compressed air and a visual check was made to ensure that the surface was free of any abrasive. This guaranteed that all abrasive residues were removed and that the bond strength was not impaired by contamination. Alternatively, the samples could have been cleaned with air-water spray or in an ultrasonic bath after sandblasting (analogous to Tekçe et al. [29]). We chose the "dry" method in order to avoid possible interactions due to moisture accumulation in the retentive surface.

With regard to light-curing of the composite cement, an exposure time of 10 seconds per mm of ceramic and segment at a light output of ≥ 1000 mW/cm² is recommended [12], while light-curing for 20 seconds per surface is recommended for the self-adhesive cement [1]. The employed light-curing protocol (see Materials and Methods section) ensured that each surface was sufficiently cured.

In the context of this study, the bond strength of various cements to a printable composite material was tested using the microtensile test [20, 21]. For our investigation, we chose stick-shaped rather than hourglass-shaped test specimens because the stick-shaped specimens can be produced by two cuts only in the x and y direction without further manipulation at the interface [4].

4.2 Discussion of results

Since there is currently no comparable data from microtensile tests for 3D printable composites in the literature, we can only compare our results with CAD/CAM composites; this includes hybrid ceramics such as Lava Ultimate (Fa. 3M Deutschland GmbH, Neuss, Germany), Vita Enamic (Fa. Vita Zahnfabrik, Bad Säckingen, Germany) or Cerasmart (Fa. GC Europe N.V., Leuven, Belgium) which can be used for permanent indirect restorations.

Peumans et al. tested Lava Ultimate and Vita Enamic in combination with different types of pretreatment and 2 composite cements (Panavia SAC and Clearfil Esthetic Cement) [22]. However, in contrast to our study, grain sizes of 27 µm were used for sandblasting with aluminum oxide. The type of silane used for chemical pretreatment was also Monobond Plus. For Lava Ultimate, the mechanical pretreatment (either Cojet or sandblasting with Al_2O_3) had a significant influence on the experimental results. Despite the smaller particle size of aluminum oxide compared to our experimental setup, the study also confirms that surface modifications lead to an increase in bond strength. Similar results were attained after pretreatment of 3 different CAD/CAM composites (Cerasmart, Lava Ultimate and Vita Enamic) [29]. Regardless of the type of CAD/CAM material, a significant increase in bond strength was achieved initially by sandblasting with aluminum oxide (27 as well as 50 µm) in combination with a dual-curing adhesive luting cement. We found a similar effect in our study for the composite cement. For the CAD/CAM composite Katana Avencia (Katana Avencia Block, Kuraray Noritake, Tokyo, Japan), the use of 50 µm Al_2O_3 also led to a significant increase in bond strength [3]. Depending on the type of surface pretreatment, an increase in pressure during sandblasting (0.1 vs. 0.2 MPa) either led to a decrease or increase in adhesion, or did not have significant effects [3]. The pressure used in our study was 1.5 bar (corresponding to 0.15 MPa), which is exactly between the pressures used by Ali et al. [3]. Initially, it led to a significant increase in bond strength for both the resin-modified glass ionomer cement and the composite cement when compared to sodium-bicarbonate glass pretreatment. When pretreating Lava Ultimate blocks with 50 µm Al_2O_3 at a pressure of 0.2 MPa, a composite cement

Group	Mean	Standard Deviation	n/ "zero bonds"	Significance level	Fracture pattern in %
FC_NAT_IN	6.76	1.74	48	b	79/0/0/21
FC_NAT_TC	7.12	2.96	47/1	b	87/0/0/13
FC_NAT_6M	2.94	1.25	48	a	0/0/0/100
FC_ALU_IN	11.36	2.73	48	c	65/0/0/35
FC_ALU_TC	9.94	2.36	48	bc	75/0/0/25
FC_ALU_6M	2.95	1.10	48	a	0/0/0/100
RXU_NAT_IN	20.53	5.58	48	ed	94/0/6/0
RXU_NAT_TC	21.09	6.19	48	ed	98/0/0/2
RXU_NAT_6M	11.25	4.86	48	c	100/0/0/0
RXU_ALU_IN	23.20	4.11	40	e	75/0/25/0
RXU_ALU_TC	21.25	2.93	48	ed	94/0/4/2
RXU_ALU_6M	33.75	4.94	48	gf	58.3/2.1/8.3/31.3
VAR_NAT_IN	22.71	4.19	48	e	67/0/29/4
VAR_NAT_TC	21.22	3.74	48	ed	55/9/4/32
VAR_NAT_6M	18.95	4.15	47	d	74.5/0.0/2.1/23.4
VAR_ALU_IN	31.45	9.84	43	f	60/0/26/14
VAR_ALU_TC	36.59	5.04	45	g	67/0/31/2
VAR_ALU_6M	43.61	7.22	47	h	55/0/34/11

Table 3 Mean values in MPa and standard deviation. n = number of sticks tested. fracture patterns (adhesive/cohesive cement/cohesive composite/mixed) in %
(Fig. 1–3. Tab. 1–3: S. Pfeffer, A.-K. Lührs)

showed significantly higher bond strength than a self-adhesive material [26]. This result is comparable with our findings, as significantly higher microtensile bond strength was achieved for the composite cement in comparison to the self-adhesive material after sandblasting, both initially and after aging. However, the study also showed that when identical cements are used, a clear influence of the restoration material exists [26].

Taking into account short-term water storage (30 days), surface treatment by means of sandblasting could lead to a significant increase in bond strength for a self-adhesive material [9]. In contrast, in our study, additional sandblasting did not significantly affect the bond strength of the self-adhesive material to the printable composite initially and after TC.

When comparing different studies, it is essential to consider that the results are highly dependent on the design and methodology used in the respective study (material to be tested, type of pretreatment, aging process, size and shape of test specimens, etc.). Besides the existing differences to our methodology, the printable composite we examined has to be classified as a new class of material, and thus is an additional factor influencing the results.

Apart from scientific publications presenting the results of single studies, a meta-analysis with the topic "Resin Bond to Indirect Composite and New Ceramic/Polymer Materials: A Review of the Literature" could show that surface treatment

with aluminum oxide of 50 µm particle size is the most effective method for roughening the surface of indirect composite materials [27]. Also, pretreatment with a silane leads to improved adhesive bond strength [7].

The results of our study showed that the highest bond strength to the printable composite was achieved, using the adhesive composite cement in combination with a silane and additional pretreatment of the samples with aluminum oxide. Besides mechanical pretreatment, another reason for this result may be the additional use of a multifunctional primer (Monobond Plus), which contains 3 functional methacrylates (silane methacrylate, phosphoric acid methacrylate and sulfide methacrylate). This additional chemical pretreatment helps to attain a stable, adhesive and long-term bond to all indirect restorative materials [15].

With regard to fracture analysis, it is remarkable that cohesive fractures occurring only in the luting cement are the smallest part of the overall distribution (0.59 %). This can be explained by the fact that the intrinsic strength of the cement is higher than the adhesive bond of the respective specimens to the printable composite material, as fractures occur more often at the interface than in the cement (Table 3).

5. Conclusion

The highest bond strength to a printable composite was attained with a self-adhesive resin cement and composite cement. By sandblasting the surface with aluminum oxide, a significant increase in the composite cement's bond strength could be measured both initially as well as after TC and water storage. However, numerous other factors are decisive for long-term clinical success, including adhesion to the tooth structure, the flexural strength of the restorative material used and the preparation design.

Conflicts of Interest

This study was financially supported by BEGO Bremer Goldschlägerei Wilh. Herbst GmbH & Co. KG, Bremen, Germany.

References

1. 3M ESPE AG: Technisches Produktprofil RelyX Unicem. http://multimedia.3m.com/mws/media/205462O/relyx-unicem-technical-profile-de.pdf (last access on 23 September 2019)

2. Alharbi N, Wismeijer D, Osman R: Additive manufacturing techniques in prosthodontics: where do we currently stand? A critical review. Int J Prosthodont 2017; 30: 474–484

3. Ali A, Takagaki T, Nikaido T, Abdou A, Tagami J: Influence of ambient air and different surface treatments on the bonding performance of a CAD/CAM composite block. J Adhes Dent 2018; 20: 317–324

4. Armstrong S, Breschi L, Özcan M, Pfefferkorn F, Ferrari M, Van Meerbeek B: Academy of dental materials guidance on in vitro testing of dental composite bonding effectiveness to dentin/enamel using micro-tensile bond strength (µTBS) approach. Dent Mater 2016; 33: 133–143

5. Barazanchi A, Li KC, Al-Amleh B, Lyons K, Waddell JN: Additive technology: update on current materials and applications in dentistry. J Prosthodont 2017; 26: 156–163

6. BEGO Bremer Goldschlägerei Wilh. Herbst GmbH & Co. KG: Personal communication with the company BEGO on 10 January 2020

7. da Costa TRF, Serrano A, Atman APF, Loguercio A, Reis A: Durability of composite repair using different surface treatments. J Dent 2012; 40: 513–521

8. El Zohairy A, De Gee A, Mohsen M, Feilzer A: Microtensile bond strength testing of luting cements to prefabricated CAD/CAM ceramic and composite blocks. Dent Mater 2003; 19: 575–583

9. Elsaka S: Bond strength of novel CAD/CAM restorative materials to self-adhesive resin cement: the effect of surface treatments. J Adhes Dent 2014; 16: 531–540

10. Fasbinder DJ: Materials for chairside CAD/CAM restorations. Compend Contin Educ Dent 2010; 31: 702–704, 706, 708–709

11. Ghavami-Lahiji M, Firouzmanesh M, Bagheri H, Jafarzadeh Kashi TS, Razazpour F, Behroozibakhsh M: The effect of thermocycling on the degree of conversion and mechanical properties of a microhybrid dental resin composite. Restor Dent Endod 2018; 43: e26

12. Ivoclar Vivadent AG: Gebrauchsinformation Variolink Esthetic DC, www.ivoclarvivadent.de/mam/celum/celum_assets/9516039110686_variolink-esthetic1variolink-esthetic-dc-1.pdf?2 (last access on 02 September 2019)

13. Kassotakis E, Stavridakis M, Bortolotto T, Ardu S, Krejci I: Evaluation of the effect of different surface treatments on luting CAD/CAM composite resin overlay workpieces. J Adhes Dent 2015; 17: 521–528

14. Lise DP, Van Ende A, De Munck J, Vieira L, Baratieri LN, Van Meerbeek B: Microtensile bond strength of composite cement to novel CAD/CAM materials as a function of surface treatment and aging. Oper Dent 2017; 42: 73–81

15. 15. MASSIVE ART WebServices GmbH: Monobond, Ivoclar Vivadent, www.ivoclarvivadent.com/de/p/zahnarzt/produkte/befestigungmaterialien/haftvermittler-befestigungsmaterial-zu-restauration/monobond-plus, (last access on 20 July 2019)

16. MatWeb: Internetseite: MatWeb – Material Property Data, http://www.matweb.com/search/DataSheet.aspx?MatGUID=c8c56ad547ae4cfabad15977bfb537f1&ckck=1 (last access on 30 January 2020)

17. Mörmann W: The evolution of the CEREC system. J Am Dent Assoc 2006; 137: 7–13

18. Mount GJ: Buonocore Memorial Lecture. Glass-ionomer cements: past, present and future. Oper Dent 1994; 19: 82–90

19. Oilo G, Jørgensen KD: The influence of surface roughness on the retentive ability of two dental luting cements. J Oral Rehabil 1978; 5: 377–389

20. Pashley DH, Carvalho RM, Sano H et al.: The microtensile bond test: a review. J Adhes Dent 1999; 1: 299–309

21. Pashley DH, Sano H, Ciucchi B, Yoshiyama M, Carvalho RM: Adhesion testing of dentin bonding agents: a review. Dent Mater 1995; 11: 117–125

22. Peumans M, Valjakova E, De Munck J, Mishevska C, Van Meerbeek B: Bonding effectiveness of luting composites to different CAD/CAM materials. J Adhes Dent 2016; 18: 289–302

23. Peutzfeldt A, Sahafi A, Flury S: Bonding of restorative materials to dentin with various luting agents. Oper Dent 2011; 36: 266–273

24. Revilla León M, Özcan M: Additive manufacturing technologies used for processing polymers: current status and potential application in prosthetic dentistry. J Prosthodont 2019; 28: 146–158

25. Roland B: Neue Technologien in Labor und Praxis: der 3-D-Druck. ZWR 2018; 127: 478–484

26. Sadighpour L, Geramipanah F, Ghasri Z, Neshatian M: Microtensile bond strength of CAD/CAM-fabricated polymer-ceramics to different adhesive

resin cements. Restor Dent Endod 2018; 43: e40

27. Spitznagel F, Horvath S, Guess P, Blatz M: Resin bond to indirect composite and new ceramic/polymer materials: a review of the literature. J Esthet Restor Dent 2014; 26: 382–393

28. Strub J, Rekow ED, Witkowski S: Computer-aided design and fabrication of dental restorations: current systems and future possibilities. J Am Dent Assoc 2006; 137: 1289–1296

29. Tekçe N, Tuncer S, Demirci M, Kara D, Baydemir C: Microtensile bond strength of CAD/CAM resin blocks to dual-cure adhesive cement: the effect of different sandblasting procedures. J Prosthodont 2019; 28: e485–e490

30. Torabi K, Farjood E, Hamedani S: Rapid prototyping technologies and their applications in prosthodontics, a review of literature. J Dent (Shiraz) 2015; 16: 1–9

31. van Noort R: The future of dental devices is digital. Dent Mater 2012; 28: 3–12

(Photo: Anne-Katrin Lührs)

(Photo: Stephanie Pfeffer)

PD DR. ANNE-KATRIN LÜHRS
Department of Conservative Dentistry, Periodontology and Preventive Dentistry, OE 7740,
Hannover Medical School
Carl-Neuberg-Str. 1; 30625 Hannover
Lührs.Anne-Katrin@mh-hannover.de

STEPHANIE PFEFFER
Department of Conservative Dentistry, Periodontology and Preventive Dentistry, OE 7740,
Hannover Medical School
Carl-Neuberg-Str. 1
30625 Hannover