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INFLUENCE OF DIFFERENT SURFACE TREATMENTS OF CAD/CAM HYBRID NANOCERAMICS CROWNS ON BOND STRENGTH OF RESIN COMPOSITE CEMENT

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Abstract: Introduction: Urgent demand for high-esthetic material, which at the same time has the possibility of absorption of mastication stress, has led to the technological development of hybrid nanoceramics used in CAD / CAM technology.

Aim: The aim of the study was to evaluate the effects of different surface modification of hybrid nanoceramic crowns on the quality of the cement retention and the influence of the mastication stress after one year of function.

Material and methods: 50 hybrid nanoceramic CAD/CAM crowns (CERASMART, GC) are cemented on titanium implant abutments with self-adhesive resin cement (G-CEM, LinkAce). The samples were divided into five main groups according to surface treatment (n=10): I (sandblasted with 50 microns Al_2O_3), II (treated with CERAMIC PRIMER II, GC), III (treated with 5% hydrofluoric acid), IV (treated with combination of 5% hydrofluoric acid and CERAMIC PRIMER II), V (control, non-treated group). The samples were storaged during 24 hours at 37°C, thermocycled and loaded under 10 000 mechanical cycles loads (simulation of 12 months of function). Retention forces measured in Universal testing machine. The data were represented as mean ± standard deviation, and for statistical analysis ANOVA test was used.

Results: The highest initial retention force was demonstrated in the group IV (6.99±1.18), followed by group I (6.22±1.29), group III (5,97±1,25), group II (5,86±1,17) and control group samples (4.92±1.19). A statistically significant decline in retention force was recorded in all tested groups, with the lowest decrease observed in samples treated with a combination of 5% hydrofluoric acid and CERAMIC PRIMER II (6.08 ± 1.03).

Conclusion: Mechanical and chemical surface modification can strongly influence the retentions between resin cement and hybrid nanoceramics. The results from this study are suggesting that the most efficient clinical outcome is the combination of 5% hidrofluoric acid and CERAMIC PRIMER II.

Keywords: hybrid nanoceramics; surface treatments; termocycling; mechanical cycle loading; cementation; cement retention.

1. INTRODUCTION

High esthetic demands of contemporary implantoprosthetic restorations have caused introducing completely ceramic restorations into dental practice. Ceramic as a structural material satisfies completely the required esthetic parameters, and although it has been used in dental implantoprosthetics as a structural material, shortcomings in the sense of brittleness and low flexural strength are limiting its clinical application and there are still attempts to eliminate them. With the appearance of the new generation of monolithic, machine processed, hybrid materials, these shortcomings have been eliminated. The

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above mentioned materials combine the advantages of composite and glass-ceramic materials and have a relatively high flexural strength, modulus of resistance and low flexural modulus [1]. In contrast to a natural tooth, which possesses the physiological mechanism of amortization of masticatory forces, due to its structure and modulus of dentin elasticity, as well as the system of periodontium, which beside the amortization of forces transfers the pressure equally on the surrounding bones, the ankylosed implant, attached to the bone, transfers all the load directly onto the bone and a great part of load is generated within the complex implant-abutment-restoration. This generation of load, if one takes into consideration the characteristic of low flexural strength and fragility of ceramics, leads to the appearance of fractures within the restoration. By combining Young's elasticity module of composite materials, which is similar to dentin with good esthetic performance of ceramics, an ideal restoration material would be obtained. On the basis of this kind of thinking, ceramics infiltrated by the composite was developed, and it shows characteristics similar to the structure of natural teeth.

The new type of hybrid ceramics was developed for the usage within the CAD/CAM technology, in the form of blocks, which were produced in industrial, strictly controlled conditions, and therefore, the performances of materials are significantly improved in comparison to the material obtained in the conventional laboratory processes [2]. These materials combine improved properties of ceramics, such as permanence and color stability, with the properties of composite materials, such as the improved elasticity module, increased flexural strength and the level of abrasiveness adapted to the natural tooth [3−4]. Several types of manufactured, synthesized blocks for CAD/CAM technology have appeared on the market by combining ceramics and composite: Vita Enamic (Vita Zahnfabrik, Bad Sackingen, Germany), Lava Ultimate (3M-ESPE, Seefeld, Germany), and GC Cerasmart (GC Dental Products, Leuven, Belgium). Essentially, it is the material, which is primarily ceramics, manufactured with nanomers and nanoclusters with the percentage of ceramics 80 wt% on average. Nanomers are silica or zirconia with the cell's diameter of 20 nm and 4-11 nm. This material, in accordance with the demands of biomimetic imitation of nature, shows equal resistance to fractures as glass ceramics and basically it is in balance with the structure of enamel with the elasticity module similar to dentin [5]. Technological process of manufacturing these materials goes in two directions: porous, presintered ceramics is conditioned, and then its infiltration with polymers is performed, or the polymer is mixed directly with the ceramics filler. Due to its good performances, composite cements are bonds, which are chosen in contemporary implantoprosthetics. These cements have exceptionally good mechanical properties; achieve high retention, and due to the resin they have good marginal sealing; they are resistant to changes of pH; they minimally soluble in the oral cavity and they accomplish high esthetic standards [6]. The estimation of usage of composite cements in implantoprosthetics has been the topic of numerous researches [7−9].

Repeated contact stress during mastication and temperature fluctuation can lead to the fatigue of cement material and its degradation and dissolution. The process of aging, beside the change of internal characteristics of material, significantly influences the value of force with which the restoration is connected to the abutment. In the light of clinical application, weaker mechanical bond of the restoration and implant abutment can result in opening the marginal seal, cement weakening and decementing of the restoration. The quality of the bond between the composite cement and abutment is at the beginning smaller in comparison with the bond between cement and natural tooth, and therefore the speed of degradation, that is, cement deterioration in the oral cavity is more intense in the bond between the restoration and abutment. Due to the above mentioned reason, it is necessary to use the adhesion promoters, so called primers, whose task is to improve the bond between different materials on the chemical base.

Numerous studies have proved that the way of treating the surface of ceramics before cementing has a strong influence on the strength of the composite cement bond [10−11]. Micromechanical retention can be improved through sandblasting or acid etching, whereas the means for silanization provides the chemical bond. With the aim of improving the bond between the composite cement and ceramics, numerous methods for the preparation of bonding surface, which improve the chemical and micromechanical retention, have been recommended [12−13].

On the other hand, composite materials include two stages, inorganic ceramics/glass filler and polymer matrix, which can be cross-linked or linear polymer based. It is known that binding of composite materials for cross-linked polymers is a great challenge, while linear polymers are easier for binding [13]. Generally, all composite cements are based on adhesive binding with the surface, which demands the adequate preparation of binding surface. The preparation of material's surface for binding the composite cement, in accordance with the characteristics of materials inside the hybrid ceramics, is more complex in comparison to pure ceramic and composite materials. Although the influence of the way of treating binding surfaces of titanium and different types of ceramics, from which abutment and implant supported restorations are made, on the quality of the bond with the composite cement has been analyzed in numerous studies, data about the influence of the way of treating the binding surface on the quality of bond CAD/CAM of nanohybrid restorations and composite cement are limited.

There are not many studies in the world about procedures of treating the surface of hybrid ceramics before cementing, but the increasing usage of hybrid ceramics implies the need to define the directives and protocol of surface preparation [14−15]. The aim of this in vitro study is the evaluation of the effect of different treatments of the surface of nanohybrid ceramics and influence of masticatory load during one year of function on the strength of the bond with composite cement. The null hypothesis of this study was: 1) The way of treating the surface of hybrid nanoceramics influences the strength and quality of the composite cement bond; 2) Exposure to masticatory load and temperature fluctuations influences the quality of the bond between nanoceramics and composite cement. 3) Decrease of retention force depends on the number of masticatory cycles and the way of treating the binding surface before cementing.

2. MATERIAL AND METHOD

In this study, 50 experimental models were used, and they were made as the combination of Implant replica Nob Rpl NP and titanium abutment (Easy abutment), on which restorations milled of hybrid nanoceramics blocks CERASMART, GC (Figure 1) were fixed with dual-cured composite cement (GC LINK Ace).

Figure 1. Experimental sample (titanium abutment and restoration made of hybrid ceramics CERASMART, GC.

The titanium abutment was fixed with the force of 35 n/cm with the moment key for the implant replica. Scanning of samples was performed with the scanner DD Argus M2 HD Dental Scanner, Dental Direct, GmbH.

Restorations were designed in Exo CAD unit of the CAD/CAM system and then milled from hybrid nanoceramics CERASMART, GC blocks. With the aim of standardizing the samples, occlusal 2/3 restorations were milled according to the model of Frasaco tooth, the lower second premolar. With the aim of preventing the break-through of cement into the interior of the abutment, the access channel for the screw was closed with the help of PTF tape.

The samples were divided into 5 experimental groups (n=10), which were treated in different ways before cementing (table 1).

Table 1. Experimental groups

GROUP	SURFACE TREATMENT
Group 1. Samples treated by sandblasting (SB)	Sandblasting with Al_2O_3 particles (50 microns), from a distance of 10 mm, for 20 seconds, at a pressure of 0.2 Mpa. After sandblasting, it was cleansed from the residual particles.
Group 2. Samples treated by Ceramic primer (CP)	Surface silanization by applying a thin layer of Ceramic Primer II. After 60 seconds, the surface is dried by air jets.
Group 3. Samples treated by hydrofluoric acid (HF)	Surface treatment by 5% hydrofluoric acid (HF; IPS Ceramic Etching Gel 5%, Ivoclar Vivadent, Schaan, Liechtenstein) for 60 seconds, rinsed with water jets for 60 seconds and dried by air jets for 20 seconds.
Group 4. Samples treated with the combination of hydrofluoric acid and silane (HF+CP)	Surface treatment by 5% hydrofluoric acid (HF), with the same protocol as in group 3, after that silanization was done by Ceramic Primer II, applying the same protocol as in group 2.
Group 5. non-treated, control group (C)	Non-treated samples.

After the preparation of the surface, all samples were cemented in a uniform way with a dual-cured composite cement G-CEM LinkAce® GC. The restoration with cement is, after placing onto the abutment, on the hydraulic press, under the controlled continual pressure of 5 kg, after which the initial light polymerization of cement is performed in the area of the marginal seal lasting three seconds. Gummy consistency makes the removal of cement excess in one piece without damaging the area of marginal seal easier. After the finished process of cementing, examples of all four experimental groups are stored during the next 24 hours in the conditions of 100% humidity and temperature of 37^o in order to make the conditions more similar to those in the oral cavity.

Afterwards, with the aim of simulating masticatory load, to which the restoration is exposed to in the oral cavity, the samples were exposed to cycles of mechanical cyclic load, whose number corresponded to the period of simulation of function in the oral cavity (simulation 6 and 12 months of function). Inside each experimental group, two cycles of testing were performed according to the previously established schedule (table 1).

Retention force was measured with the Universal testing machine. 40 measurements were performed in total, 10 in each experimental group.

Materials, which were used in the study, were presented in Table 2.

Table 2. Materials used in the study

MATERIAL	TYPE	MANUFACTURER	COMPOSITION
CERASMART	Hybrid nanoceramic CAD-CAM block	GC Corp., Tokyo, Japan	Silica (20 nm) and barium glass (300 nm) nanoparticles (71 wt.%) Polymers (29%) of Bis-MEPP, UDMA, and DMA
G-CEM LinkAce	dual-cure self-adhesive universal resin cement, with high content of self adhesive components	GC Corp., Tokyo, Japan	Paste A: UDMA 10%-20%, Ymethacryloxypropyltrimethoxysilane .2.5% Paste B: UDMA 25%-50%, methacryloxypropyltrimethoxysilane .2.5-10%, A,a-dimethylbenzylhydroperoxide 1
Ceramic Primer II	(ceramic and composite bonding primer)	GC Corp., Tokyo, Japan	90%-100% ethanol, 1%-5% 2,20 -ethylene dioxydiethyl dimethacrylate, 1%-5% methacryloyloxydecyl dihydrogen phosphate, ,1% (1-methylethylidene) bis[4,1-phenyleneoxy(2-hydroxy-3,1-propanediyl)] bismethacrylate. Application protocol: Applying to the ceramic surface for 2 minutes and then air drying.
HF; IPS Ceramic Etching Gel 5%,	Ceramic Etching Gel	Ivoclar Vivadent, Schaan, Liechtenstein	Aqueous solution of hydrofluoric acid (5%) Surface etching for 60 seconds, rinsed with water jets for 60 seconds and dried by air jets for 20 seconds.
Danville Aluminum Oxide	Sandblasting particles	Danville, Zurich, Switzerland	Al_2O_3 particles, 50 microns

3. RESULTS

Samples treated with the combination of hydrofluoric acid and silane show the highest initial retention force (6.99$\pm$ 1.18), and they are followed in the falling series (progression) by the samples, which were treated by sandblasting (6.22$\pm$1.29), hydrofluoric acid (5.97$\pm$1.25), silane (5.86$\pm$1.17) and non-treated, control group (4.92$\pm$1.19). After exposing the samples to thermal cycling and mechanical loading cycles, with the help of ANOVA test, statistically significant decrease of the retention force in all the examined groups of samples was observed, while the lowest decrease of retention was recorded in samples treated with the combination of hydrofluoric acid and silane (6.08$\pm$1.03). The comparison of values of experimental groups' retention forces is shown in table 3.

Table 3. The comparison of retention values in the examined samples

Experimental group		Unloaded samples	Retention force after 12 months of function	Statistical significance
Non-treated samples (C)	AC	4,92	3,4	p=0,009<0,05
	СД	1,19	0,85	
Sandblasting samples - Al_2O_3 (50 microns) (SB)	AC	6,22	4,73	p=0,009<0,05
	СД	1,29	0,9	
Samples treated with hydrofluoric acid (HF)	AC	5,97	4,89	p=0,052>0,05
	СД	1,25	0,9	
Samples treated with Ceramic Primer II (CP)	AC	5,86	4,56	p=0,019<0,05
	СД	1,17	1,03	
Samples treated by combination of 5% hydrofluoric acid (HF) and Ceramic Primer II (HF+CP)	AC	6,99	6,08	p=0,035<0,05
	СД	1,18	1,03	

Two samples from the experimental group number two (samples treated with 50 microns Al_2O_3) underwent fracture damages during testing in the Universal testing machine and they were not taken into account during statistical analysis.

Three-way ANOVA test shows that there is connection between the way of treating the surface, mechanical cyclic load and retention force of the cement ($p<0.05$). According to the results of ANOVA test, we came to conclusion that statistically significant difference ($p<0.05$) existed between the group of non-treated samples and samples treated with the combination of 5% hydrofluoric acid and silane Ceramic Primer II with the value of the retention force after the first cycle of testing (table 4, 5).

The results of Mann-Whitney U test showed a statistically significant difference between the first (0) cycle of testing and the second cycle of testing (12 months) in all experimental groups in the average retention force except the experimental group treated with hydrofluoric acid HF (table 4, 5).

Table 4. Statistical comparison of the results between the experimental groups before mechanical cyclic load and thermal cycling

	C	SB	HF	CP	HF+CP
C		0,138	0,320	0,424	0,004
SB	0,138		0,990	0,965	0,622
HF	0,320	0,990		1,000	0,344
CP	0,424	0,965	1,000		0,253
HF+CP	0,004	0,622	0,344	0,253	

Table 5. Statistical comparison of results between experimental groups after mechanical cyclic load and thermal cycling

	C	S	HF	CP	HF+CP
C		0,025	0,009	0,065	0,000
S	0,025		0,996	0,995	0,021
HF	0,009	0,996		0,938	0,053
CP	0,065	0,995	0,938		0,007
HF+CP	0,000	0,021	0,053	0,007	

*statistically significant difference exists when $p<0.05$

According to the results of ANOVA test, we came to conclusion about the existence of statistically significant difference after the second cycle of testing with the average value of retention force between the non-treated samples and samples, which were sandblasted with Al_2O_3 particles (50 microns), samples treated with silane Ceramic Primer II, samples treated with HF acid and samples treated with the combination of 5% hydrofluoric acid and Ceramic Primer II ($p<0.05$). Also, statistically significant difference was recorded between the samples treated with the combination of 5% hydrofluoric acid and silane Ceramic Primer II and samples sandblasted with Al_2O_3, as well as between the samples treated with the combination of 5% hydrofluoric acid and silane Ceramic Primer II and samples treated with Ceramic Primer II ($p<0.05$).

4. DISCUSSION

Permanence and functional efficiency of implant-supported restorations fixed with cements are determined, among other things, by the appropriate procedure of cementing, thus achieving the adequate binding of the restoration for the implant abutment and quality edge sealing.

The results of this study unambiguously showed that the way of preparing the surface for cementing influences the strength of the bond between the composite cement and hybrid ceramics, thus confirming the first hypothesis of this research. The research also showed that the protocols of material aging significantly decrease the strength of the bond between cement and hybrid ceramics, which confirms the second set hypothesis. In the world literature, there are very few official scientific studies about the influence of the ways of treating the surface of hybrid ceramic materials, which are prior to cementing [13,16−18], and therefore there are still no established protocols of preparation of these ceramics, except those recommended by the manufacturer. Hybrid ceramic-composite materials present structures with different share of ceramics and composite, with which we can explain the specificity of the preparation of their surfaces for cementing [19].

As recommended by the manufacturer, CERASMART hybrid ceramic should be treated with sandblasting of hydro-fluorine, the acid which is followed by the application of silane, Ceramic Primer II [20]. Although the equivalent application of sandblasting and hydrofluoric acid is recommended, the existing study proved that sandblasting of the surface of CERASMART surface with the particles Al_2O_3, under the pressure of 0.2 Mpa, results in higher strength of the bond between composite cement and hybrid ceramics (6.22±1.29) in comparison to the surface, which has been eroded by HF acid (5.98±1.25). Having in mind that statistically, the greatest bond strength was found in the group of samples, which were treated with the combination of HF acid and silane (6.99±1.18), it can be concluded that additional usage of silane significantly participates in the bond strength.

Campos and associates proved that the application of hydrofluoric acid is more efficient in increasing the roughness of hybrid ceramics surface (Vita Enamic) than sandblasting. The reason can be in the high content of ceramics with little participation of composite component. Glass component contained in this material is subject to dissolution when exposed to the action of hydrofluoric acid [17].

The existing study proved that sandblasting of the surface of hybrid material, which is prior to cementing, significantly increases the bond with cement from 4.92 MPa in non-treated samples to 6.22 MPa in sandblasted samples. Although some other significant studies proved that sandblasting of hybrid materials improves the bond with hybrid materials, authors point to the necessary caution when choosing the size of particles and the applied pressure of sandblasting. A rapid decrease of the bond strength in comparison to non-sandblasted samples is observed in a uniform way in Lava Ultimate material, when the pressure of abrasion is increased to 0.3 MPa [21].

The authors proved with SEM analysis and analysis of the surface roughness that the increase of surface roughness increases with the increase of the pressure of sandblasting, but it does not necessarily result in the increase of the strength of the cement bond [22,23].

In contrast to the bond between the conventional ceramics and composite cement, which shows fracture on the seal between ceramic and composite, in hybrid materials different results can be observed. Cekic-Nagas and associates [24] observed the lost of bond in 39% of samples Vita Enamic and composite cement inside the hybrid material due to the cohesive structural damages of the material, while cohesive fractures were not registered in Cerasmart samples. The bond strength was high in cohesively fractured samples. Cohesive fractures inside Vita Enamic material indicate that the bond between ceramics and cement exceeded the strength of the material itself.

The excessive pressure can cause the concentration of tension inside the material with damages inside the material and high rate of cohesive errors. When the rate of damage is high, there is a great possibility that the bond of the cement will surpass the strength of the material, and therefore, the observed decrease of the bond strength can be connected with the high pressure of abrasive particles, which weakens the fractural stability of this material, more than with the simple decrease of the strength of cement bond.

In the existing study, in 25% of samples in the group treated with 50 microns Al_2O_3 particles, there came to fractures inside the material during the application of force necessary for separating the restoration from the abutment, which confirms the findings of the above mentioned study of Kim and associates.

In contrast to this, Chen and associates found that treating with 50 microns Al_2O_3 particles of the surface of Lava Ultimate samples does not influence the fractural resistance of the material, but it is necessary to point out that the value of applied pressure was not described [25].

The usage of particles Al_2O_3 under the pressure of 0.2 MPa leads to abrasion of the surface and elimination of fillers. Due to the possibility that alumina particles damage the surface of CAD-CAM hybrid materials, the usage of glass particles is recommended rather than alumina particles [26].

The previous study about the influence of abrasion on the adhesion of two types of composite cements, including the dual-curing, self-eroding composite cement Panavia, and Lava Ultimate material, found that the bond was significantly higher in the group of samples treated with abrasion, in comparison to non-abraded group [27].

However, when after sandblasting and cleaning of the surface, the universal bond was applied, the high strength of bonding was found even in the group, which was not treated with abrasive particles.

The study of Lauvahutanon and associates, which dealt with the comparison of mechanical characteristics of commercial composite blocks with the contents of inorganic filler, ranked hybrid materials according to the content of inorganic filler: Vita > Vita Enamic > Lava Ultimate > Gradia Block > Cerasmart >Bloch HC [28].

According to SEM analysis, the contents of inorganic filler and EDS analysis, three types of structures have been observed: composite matrix with filler (BLO, CER, GRA and ULT), ceramics net structure with composite matrix (ENA), and ceramic structure (VIT).

Previous studies point to the correlation between the contents of the filler contained in the hybrid material and strength of cement bond [18−19].

Miyazaki and associates examined the relationship between the contents of the filler and strength of the bond between light polymerizing composite and dentin in in vitro study and they found that the bond strength increases with the larger amount of filler [15,29].

Therefore, the improved bond of Vita Enamic ceramics can be related to high percentage of fillers (86%) in comparison to Lava and Cerasmart ceramics (80% and 71%). Two types of hybrid ceramic structures have been tested: composite matrix with filler (Cerasmart and Lava Ultimate) and ceramic net with composite matrix (Vita Enamic).

A significant difference in the bond can be explained by the amount and micro-structural characteristics of these CAD/CAM ceramics. Also, it is possible that low strength of the bond, which was observed in CAD/CAM composite blocks (Cerasmart and Lava Ultimate), is caused by the penetration of water into the resin matrix of these blocks after two days of storing in water and thermal cycling. Furthermore, in composite material, particles of inorganic filler are submerged in polymer matrix without interconnection [30].

Therefore, materials with the ceramic net show less water absorption. SEM observation shows that there is no significant difference between the strength of the ceramics and composite bond among the samples treated with HF acid and sandblasting. However, significant difference was recorded in the microstructure of the surface in Vita Enamic, Lava Ultimate and Cerasmart materials after the treatment [24].

The results are in accordance with previous studies, which demonstrate HF treatment, as the glass phase is dissolved on the surface, the bond is established mainly with the composite resin [31].

Ceramics component is subject to eroding, while selective dissolution happens when the material is exposed to hydrofluoric acid, which results in the increase of surface roughness and better mechanical interlock with composite cement, and therefore the bond strength would be, as expected, higher in hybrid materials in which ceramic component is dominant, and which can be, therefore, efficiently abraded [32−34].

The results of the study show a stronger bond in samples treated with the combination of HF acid and silane in comparison to other applied methods. The method of isolated sandblasting is on the second place, disregarding the composite component which dominates the structure of the material. The reason can be in the additional chemical activation of the surface with silane with the content of MDP.

The bond strength decreases after the applied protocol of aging. However, the protocol of sandblasting is recommended by authors during the preparation of the surface of ceramics and composite for cementing.

In samples with surfaces treated before cementing, the decrease of the cement retention after the application of the protocol of aging was recorded in another way, as well.

As the previous studies have shown [35,33,17], ceramics and composites should not be bound by composite cement before the previous application of methods, which leads to the increase of their roughness and mechanical bond as a consequence of that.

Although hybrid nanoceramics materials present a very good solution for making restorations in implantoprosthetics, primarily due to their ability of amortization of masticatory stress and nice esthetics, current clinical experience has shown that additional caution is necessary, as well as more precise defining of the protocol of preparation of their surface for cementing. 3M ESPE has recently removed indication for the crowns for Lava Ultimate hybrid ceramics due to the recorded high rate of decementing [36−37].

Dealing with this problem, Schepke and associates reported about the high rate of decementing of digitally made restorations of composite nanoceramics (RNC, Lava Ultimate, 3M ESPE, Seefeld, Germany), cemented with composite cement (RelyX Ultimate combined with Scotchbond Universal, 3M ESPE) onto zirconium abutments (ZirDesign and ATLANTIS, DENTSPLY Implants, Mölndal, Sweden). Decementing was, during the first year of function, recorded in even 80% of restorations, disregarding the preparation of binding surfaces, which was performed according to the manufacturer's instructions. They came to conclusion that a potential explanation can be searched in the low module of flexibility of Lava Ultimate hybrid ceramics of 12 GPa and consequential separation of the restoration under stress [38]. The complex implant/abutment has the minimal resilience and most of elastic deformations happen inside the material of the restoration, thus resulting in the concentration of stress in adhesive layer. Separation happens in the area of the weakest point, the seal of zirconium abutment and cement.

An additional problem can be the fact that during the surface preparation, MDP was not used in the cement or silane content. The results of Schepke and associates are contrary to the results obtained in the existing study. The high survival rate of the bond CERASMART CAD-CAM restorations and titanium abutments in the existing study could be explained by the difference in the structure of the material. Hybrid ceramic material CERASMART, examined in this study, contains a flexible nanoceramics matrix with equal distribution of nanoceramics (71% of fillers) [39].

Due to the flexible matrix, the material shows the capacity to absorb stress, which is a desirable characteristic in implant-supported crowns. Flexural strength of CERASMART is 220 MPa – 240 MPa [39, 28], which is somewhat more than feldspat ceramics.

These are the facts that can explain significantly different results. Also, the bond of composite cement with titanium abutment has been improved by the usage of silanes with the contents of MDP, while in the work methodology of Schepke, there is no data about the treatment of the surface of zirconium abutment.

The results of the existing study showed that the value of retention force significantly increases after the usage of silane Ceramic Primer II (5.86$\pm$1.17) in comparison to non-treated samples (4.92$\pm$1.19), however, statistically significant higher decrease of retention force was recorded after aging of the samples in samples whose surface was not treated (3.4$\pm$0.85) in comparison to the group, in which silane Ceramic Primer II was applied (4.56$\pm$1.03).

Silane, which was used in this study, Ceramic Primer II contains 10-methacryloxydecyl dihydrogen phosphate (MDP), which can have an additional effect on the strength of the bond between composite cement and nanohybrid ceramics. Similarly, previous studies indicated that cements, which contain adhesive monomer (MDP), show greater bond strength in comparison to other structures [40].

In the case of improving the adhesion with silane, one should have in mind that adhesion modified by silane is subject to hydrolysis and that it comes to the degradation of interface spontaneously during plunging into water [41].

In accordance with it, samples whose surface is treated exclusively with Ceramic Primer II show the lower value of the strength of the cement bond (5.86$\pm$1.17) in comparison to samples treated with HF acid (5.97$\pm$ 1.25), but that difference is not statistically significant. However, after the exposure of samples to mechanical cyclic load, humidity and thermal fluctuations, there comes to the higher decrease of bond value in samples treated with Ceramic Primer II in comparison to samples treated with HF.

Dual-curing cement was used in the study, because previous studies showed that this cement is more efficient in comparison to autopolymerizing cement [42−43]. The universal bond was used as a primer because it contains different functional components, such as 10-methacryloxydecyl dihydrogen phosphate (MDP) or silane, as addition to components, which were present in the previous widely used primers. Moreover, in previous studies regarding the bond between composites and hybrid ceramics, it was found that the bond is stronger when the adhesive solution contains MDP than when it contains only silane [24]. It is deemed that silane can improve the bond because hybrid ceramics also contains silica fillers. In this study, the bond strength decreases significantly after thermal cycling, in all the examined groups, which demands the acceptance of the second null hypothesis. After storing the samples in the water environment and exposure to thermal fluctuations, the bond between ceramic parts of hybrid material and composite cement may be endangered. In accordance with this study, the previous study of Campos and associates examined the effect of thermal cycling on the strength of the bond between CAD/CAM ceramics and composite cement, and it was concluded that the protocol of aging significantly decreases the strength of the cement bond [17]. Other studies confirmed that the strength of this bond drastically decreases after aging and storing of samples in water [17,44−45]. The decrease of bond strength after thermal cycling can be connected with the small molecular size and high molar water concentration, which can negatively influence the thermal stability of polymers. It comes to the penetration of water into small spaces between polymer chains of functional groups, resulting in the decrease of thermal stability of polymers and causing plastification [47−48]. These conditions can cause plastification and possibly hydrolytic degradation of composite cement [46−47]. Therefore, the permanence of the bond between ceramics and composite material must be additionally protected by the previous preparation of the surface, which is based on the increase of roughness [48]. The structure of ceramics itself determines the manner of preparing the binding surface. It has been proved that eroding of the surface by hydrofluoric acid and silanization significantly improve the bond with the cement [17]. Different compositions of blocks, structures of fillers, compositions, type, concentration and mechanical characteristics between different types of hybrid ceramics may result in the fact that surface treatments have different effects on the bond strength in different types of hybrid materials, although the same protocol of surface preparation was applied [17].

The lowest retention value in the group of samples with non-treated surface before and after aging clearly points that the pre-treatment of surface is necessary for achieving quality and clinically acceptable bond between cement and hybrid ceramics.

The limit of the study is the fact that only one type of hybrid material has been included in the study, and as a consequence, the presented results are valid only for CERASMART and must be interpreted carefully in relation to other types of hybrid ceramics.

5. CONCLUSION

There have been a few scientific studies, which dealt with the problem of adhesion of composite cement on the surface of hybrid ceramics, in the world so far, but the expansive growth of the usage of hybrid ceramics imposes the need for defining clear cementing protocols. The way of preparing the surface for cementing significantly influences the strength of the bond between composite cement and nanohybrid material. Abrading the surface with hydrofluoric acid or sandblasting, followed by chemical improvement of the bond with a suitable silane can be recommended. However, additional research is necessary in order to define the appropriate size of particles and applied pressure of sandblasting. Disregarding the way of surface preparation, aging of the material leads to the decrease of the strength of the bond between cement and nanohybrid material, but the intensity of the value decrease differs depending on the applied way of surface preparation. The lowest decrease of value is shown in the samples treated with the combination of hydrofluoric acid and silane. Additional researches are necessary about the influence of the factors of oral cavity on the bond strength, in the sense of increasing the quantity of mechanical cyclic load and thermal fluctuations.

6. ACKNOWLEDGMENT

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УТИЦАЈ ПОВРШИНСКОГ ТРЕТМАНА CAD-CAM КРУНА ИЗРАЂЕНИХ ОД ХИБРИДНЕ НАНОКЕРАМИКЕ НА КВАЛИТЕТ ВЕЗЕ СА КОМПОЗИТНИМ ЦЕМЕНТОМ

Сажетак: Увод: Високи естетски захтјеви комбиновани са потребом за материјалом који има могућност апсорпције стреса како би се постигла пасивност и смањило неадекватно оптерећење импланта у току мастикације условио је технолошки развој хибридних нанокерамика у CAD/CAM технологији.

Циљ: Циљ ове студије је био испитати утицај различитих начина припреме површине надокнаде на квалитет везе композитног цемента, као и утицај мастикаторних сила у току прве године функције.

Материјал и метод: У студији је коришћено 50 експерименталних модела сачињених као комбинација имплант реплика Nob Rpl NP, титанијумских абатмента, на које су композитним цементом GC LINK Ace фиксиране надокнаде исфрезоване од хибридних нанокерамичких блокова CERASMART, GC. Узорци су подијељени у пет експерименталних група (н = 10), које су прије цементирања третиране на различите начине: 1. пјескарање честицама Al_2O_3 (50 микрона); 2. силанизација са Ceramic Primer II; 3. 5% хидрофлуорична киселина HF; 4. комбинација силана Ceramic Primer II и 5% флуороводоничне киселине; 5. контролна група, нетретирани узорци. Узорци су похрањени у условима влаге у току 24 сата на 37°C и подвргнути механичким цикличним оптерећењима (симулација 6 и 12 мјесеци функције). Ретенциона сила је мјерена у универзалној машини за кидање.

Резултати: Највишу иницијалну ретенциону силу показују узорци третирани комбинацијом флуороводоничне киселине и силана (6,99±1,18) а слиједе га у опадајућем низу група узорака третираних пјескарењем (6,22±1,29), хидрофлуороводоничном киселином (5,97±1,25), силаном (5,86±1,17) и нетретирана, контролна група (4,92±1,19). Након излагања узорака термоциклирању и МЦО, употребом ANOVA теста, забиљежен је статистички значајан пад ретенционе силе код свих испитиваних група узорака, при чему се најмањи пад ретенције биљежи код узорака третираних комбинацијом флуороводоничне киселине и силана (6,08±1,03).

Закључак: Механичка и хемијска обрада површине значајно утиче на квалитет везе композитног цемента и нанохибридних надокнада, при чему се комбинација 9% флуороводоничне киселине и силана издваја као најефикаснија.

Кључне ријечи: хибридне нанокерамике, припрема површине за цементирање, механичка циклична оптерећења, квалитет везе, ретенција цемента.