Analysis of Shear Bond Strength and the Quality of the Interface Between Composite Resin and Novel Hybrid Calcium Silicate Cements

Ivanka DIMITROVA *, **Desislava TSANOVA-TOSHEVA**

Department of Conservative Dentistry, Faculty of Dental Medicine, Sofia Medical University, Sofia, Bulgaria 1, G. Sofiyski Blvd, Sofia-1431, Bulgaria

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Hybrid calcium silicate cements (HCSC) are new bioactive materials of the fourth generation with the main application as pulp capping agents and/or as liners in indirect pulp capping. The aim is to analyze the shear bond strength and the quality of the interface between a composite restorative material and a new bioactive material and other hybrid cements at the same conditions. The used pulp-capping hybrid materials: TheraCal and the new hybrid biomaterial BioCal-Cap. In this study only one type of adhesive system (Scotchbond 3M, St. Paul, MN, US) and resin-based composites (Filtek Ultimate 3M, USA) were used. For this purpose, 60 molds were prepared and divided into 4 groups. Half of them were filled with TheraCal and the other 30 with BioCal-Cap. The shear bond strength between calcium-silicate cements and the composite material was investigated. Mann-Whitney test and Wilcoxon Signed Ranks Test were used for statistical analysis of the results. In both of the materials there was no statistically significant difference in the results after the immediate and postponed placement of the composite material. Nevertheless, in both of them there was a tendency for a slight increase in shear strength in the samples which delayed the application of the restorative material. The novel hybrid material BioCal-Cap was reported to have higher shear strength values (18.06 – 20.25 MPa) at both time periods in comparison to the values for TheraCal (13.71 – 15.58 MPa). The data clearly showed that the time of the composite material placement did not affect the shear bond strength in each of the observed groups. The median value was shifted higher after the immediate composite placement, which supported one-step treatment approach to the novel hybrid material BioCal-Cap, while the TheraCal LC exhibited the opposite tendency. The adhesive layers in both hybrid cements were homogeneous, properly structured, without the presence of microcracks and gaps, and had different thicknesses at different recovery times.

Keywords: pulp-capping materials, composite material, shear bond strength, hybrid calcium silicate cement, adhesive layer.

1. INTRODUCTION

Resin-modified calcium silicate cements or Hybrid calcium silicate cements (HCSC) are new bioactive materials of the fourth generation with the main application as pulp capping agents in direct pulp capping and/or as liners in indirect pulp capping [1]. Direct pulp capping (DPC) is a biological treatment method, indicated in reversible inflammatory diseases of the dental pulp (DP), in which a suitable material with appropriate physicochemical properties is applied at the site of communication with pulp and the goal is the initiation of reparative dentinogenesis and preservation of its vitality and function [2]. Therefore, the material intended for direct contact with the DP must not only be biocompatible, but also have a bioactive capacity [3]. Biologically active materials are materials which induce specific biological activity such as the promotion of tissue regeneration, repair, reconstruction. The bioactive potential of calcium silicate cement is due to its ability to realise calcium ions and induce the formation of apatite like substance [4]. By nature, hybrid cements are a combination of Portland cement (PC) and resin [5]. The main representative of this group is TheraCal LC [6], introduced into dental practice in 2010. Its composition is 45 % PC type III, 40 wt.% resin, and 10 % radiopaque agent – bismuth oxide. Recently, Bisco introduced a new dual resin modified calcium silicate cement TheraCal PT, with basic indication pulpotomy in pediatric dentistry. It consists of synthetic Portland Cement and polyethylene glycol dimethacrylate (10 – 30 %) and Bis-GMA (5 – 10 %) resin matrix [6].

A new BioCal Cap [7] was introduced into clinical practice in 2019. According to the manufacturer, the material is a combination of 35 – 45 wt.% hydrophilic resin, PC and barium sulfate 7 – 12 %. BioCal Cap similar to TheraCal is available in syringes in a paste form. In the literature, however, there are no studies and no available information about its physico-chemical properties.

Calcium silicate cements (CSCs) are hydraulic materials by nature and require the presence of water for the proper hydration process, but with TheraCal it is absent and supplied by the contact environment [1, 8].

In clinical dental practice the success rates of the various types of calcium silicate cements are ranged from 78 – 90 % [9]. According to Peskersoy, the clinical success of MTA and Biodentine such as pulp capping agents after 36 months follow up is 86.3 % and 79.4 % respectively [10]. There are a few reported results of the clinical performance of HCSC [10]. The clinical success of the TheraCal group is 72.1 %, success provided at pulp exposure size below,

*Corresponding author. Tel.: +359 887838973.
E-mail: *vanja_ves@abv.bg* (I. Dimitrova)

5 mm. In contrast, other authors report a rate of success of 85.5 % after the application of Theracal LC [11].

Bond strength and the joint between composite resin material and HCSC are critical factor for a favourable long-term outcome. The strength of the adhesive bond between HCSC and dentin and between HCSC and the used composite materials (CM) for the final restoration of the tooth is of utmost importance for a good healing process and the durability of the restoration [12, 13].

There is a lack of guidance in the dental literature on the appropriate timing of permanent restoration placement in cases of treatment and the use of hybrid calcium silicate cements. There are conflicting data regarding the preferable bonding protocol (self-etch or total-etch) [14, 15, 16, 17]. Some studies conclude that self-etch provides higher bond strength than etch–and–rinse; in contrast, others find just the opposite and third- the adhesive protocol is irrelevant. In the literature, the studies concerning the bond strength between TheraCal and the used composite material are insufficient, and the results obtained are contradictory [18 – 21].

The strength of the connection between the HCSC and the restorative material depends on many different factors such as the qualities of the cements and the type of restorative material themselves, the type of adhesive system used, temperature, available moisture, etc. [13]. A minimum adhesive bond ranging from 17 – 20 MPa was found to be fully sufficient to resist masticatory pressure forces and ensure the durability of the restoration [20]. A quality adhesive bond between the pulp capping agent and the restorative material is a condition which provides an adequate seal without gaps as well as prevents bacterial penetration [22].

The purpose of this study is to compare and analyse the shear strength and the quality of the adhesive layer at the interface of two pulp capping materials: (2 different types hybrid) under the same conditions in terms of applying the same adhesive system and restorative material placed at different times: immediately after the setting of the pulp capping agent and postponed after 2 weeks. The aim is to determine the proper time for the restorative procedure in cases of treatment with hybrid calcium silicate cements such as pulp capping agents and whether delayed restoration leads to an increase in the shear bond strength between them. The first null hypothesis was that there were no statistically significant differences in shear bond strength value between the tested hybrid cements at different time restoration periods. The second hypothesis was that there were statistically significant differences in shear bond strength value.

2. EXPERIMENTAL PROCEDURES

In the present study, 60 metal molds with a diameter of 5 mm and 2 mm height were used. All the procedures described below were performed by one dentist and the purpose was to standardize the conditions. The study was carried out in four groups of 15 samples in each as follows:

I group – BioCal Cap (Harvard Dental International) immediately after its setting, a composite material was placed;

II group – BioCal Cap (Harvard Dental International) postponed, 2 weeks after setting a composite material was placed;

III group – TheraCal (Bisco, Schamurg, IL, USA), immediately after its setting, a composite material was placed;

IV group – TheraCal (Bisco, Schamurg, IL, USA), postponed, 2 weeks after setting a composite material was placed.

Table 1. Tested materials

Brand composition	Manufacturer	Lot No.	Indications
TheraCal LC Composition information is missing in the instructions for use	BiscoSchamurg IL, USA	2000003449 2000007311	Direct pulp capping; Indirect pulp capping in deep preparation
Bio Cal Cap Composition information is missing in the instructions for use	Harvard Dental International Germany	92001694 92107188 91905310	Direct pulp capping; Indirect pulp capping in deep preparation

2.1. PREPARATION OF THE SPECIMENS

For all the groups, a total of 60 samples, Biocal-Cap and TheraCal hybrid cement were prepared and used. TheraCal LC was set by light polymerization for 20 seconds and the other material Biocal-Cal Cap for 40 seconds (a layer thickness 1 mm). The light tip of the lamp was held at a distance of 1 mm and at right angles to the surface of the samples.

For the samples a subsequent surface was treated by applying and spreading a universal adhesive system (Scotchbond 3Mespe, St. Paul, MN, US) in a thin layer, slightly dried and polymerised with a BlueDent Smart photopolymer lamp (BG Light Ltd., Plovdiv Bulgaria) for 20 seconds.

Restorative procedures: for the placement of the composite resin material on the pulp capping materials, additional metal cylindrical molds were made (3/2 mm) which were fixed on the samples and filled with Filtek Ultimate (3M, USA).

In the samples of I and III groups the application of CRM was placed immediately after the setting of the pulp capping material and the other, the application of the restorative material was postponed for two weeks. The last two groups of samples were stored at 37 °C in thermostat conditions and moisture.

The monoblocks prepared in this way had undergone shear strength tests. The testing was carried out on an electromechanical bench for physicomechanical tests Multitest 2,5-i (Mecmesin, West Sussex UK).

2.2. METHODTEST CONDITIONS OF SHEAR BOND STRENGTH

The strength test was carried out on the LMT-100 stand (LAM Technologies Electronic Equipment, Florence, Italy) of a special device for the implementation of shear forces in the adhesive layer of the sample.

The design of the stand and its software, as well as that of the device, provided a reproducible performance of the load conditions of the test specimens. The precision of the measured displacement of the movable part of the structure was 0.001 mm. The speed of movement (load) of the test body can be set to 0.001 mm/s. The registered power was 0.1 N.

2.3. SCANNING ELECTRON MICROSCOPY EXAMINATION

Selected destroyed test samples were subjected to further examination by Scanning Electron Microscopy (SEM) (Lyra TESCAN®Brno-Kohoutovice, Czech Republic) at 20 kV. The images of the selected materials were reviewed at different magnifications from 3× to 1.000.000.

2.4. STATISTICAL ANALYSIS

The statistical analysis was done by the Mann-Whitney test and Wilcoxon Signed Ranks. The distribution of the compared variables in the individual groups was different from the normal distribution- the check was performed with the Shapiro-Wilk test. In this case, it was a nonparametric test Mann-Whithney for independent groups and the Wilcoxon Signed Ranks test for dependent groups.

The total 60 number was chosen as optimal, considering that statistical conclusions were to be drawn.

3. RESULTS

3.1. Results from the shear bond strength test

In both materials, there was no statistically significant difference in the results after the immediate and postponed placement of the composite material. There were statistical differences at $p < 0, 05$. Nevertheless, in both, there was a tendency for a slight increase in shear strength in the samples with a delayed application of the restorative material (Table 2 and Table 3), but again there was no statistically significant difference in the results.

Higher shear strength values ((18.06 – 20.25 MPa) were reported at both time periods for the novel hybrid material BioCal-Cap than those of the TheraCal ((13.71 – 15.58 MPa). The tested new hybrid cement achieved high bond strength values over 17 MPa in both time periods, values capable of withstanding masticatory stress.

The diagram (Fig. 1) represents the distribution of the strength values for both materials. For the TheraCalLC, there was a tendency for the higher displacement of the median value when immediate and postponed CRM placements were applied. This showed that it was more appropriate for the composite material to be placed two weeks after the setting of the pulp capping agent. In the new material BioCal-Cap there was the opposite tendency: the median value was shifted higher after immediate composite placement, which supported a one-step treatment approach.

Therefore, the most proper time for the placement of CM over TheraCal LC was delayed by14 days.

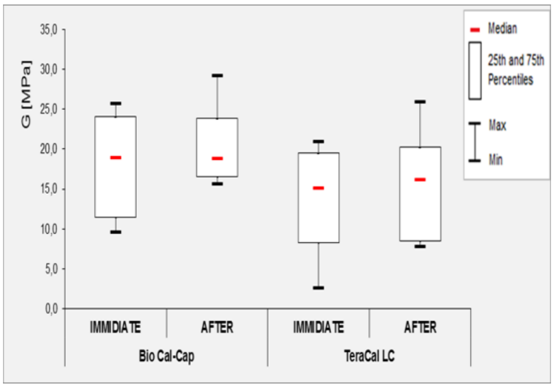

Fig. 1. Distribution of strength values for TheraCal and BioCal-Cap

In the comparison of the two materials there was no statistically significant difference in both - the immediate placement of CRM and the postponed placement ($p > 0.05$) see Table 3.

Table 3. Mann-Whitney test

	Comparison		*p*
Immidiate G, MPa	Bio Cal-Cap	TheraCal LC	0.198
After G, MPa	Bio Cal-Cap	TheraCal LC	0.096

3.2. Results from scanning electron microscopy examination

Representative SEM images are presented in Fig. 2 – Fig. 6.

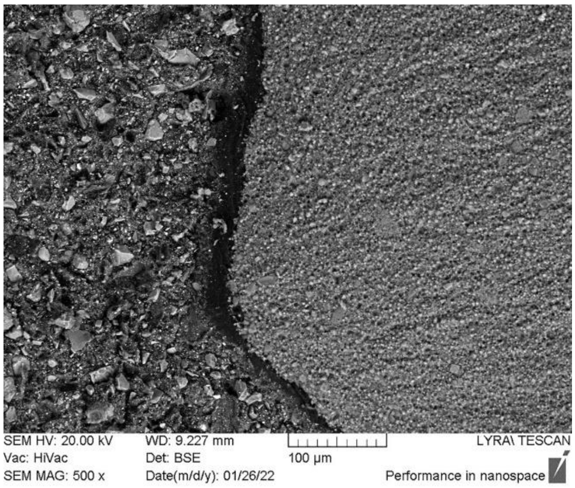

Fig. 2. Hybrid layer at BioCal Cap after immediate recovery 500^{x}

Table 2. Wilcoxon signed ranks test

Brand		N	Mean	Median	SD	Min	*p*
Bio Cal-Cap	Immidiate G, MPa	15	18.06	18.90	6.13	9.60	0.475
	After G, MPa	15	20.25	18.80	4.57	15.60	
TheraCal LC	Immidiate G, MPa	15	13.71	15.10	6.78	2.60	0.185
	After G MPa	15	15.58	16.16	6.17	7.80	

As can be seen from the presented scanograms, the hybrid layer between the PCA and CM is homogeneous, properly structured, without the presence of microcracks and gaps, and has different thicknesses (Fig. 2 – Fig. 6).

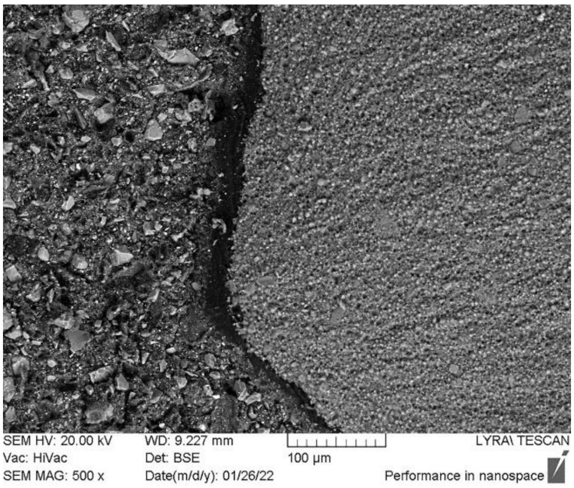

Fig. 2. Hybrid layer at BioCal Cap after immediate recovery 500^{x}

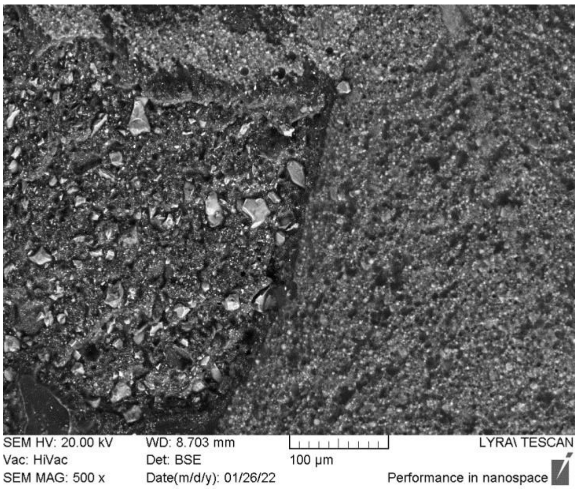

Fig. 3. Hybrid layer at BioCal Cap after postponed recovery 500^{x}

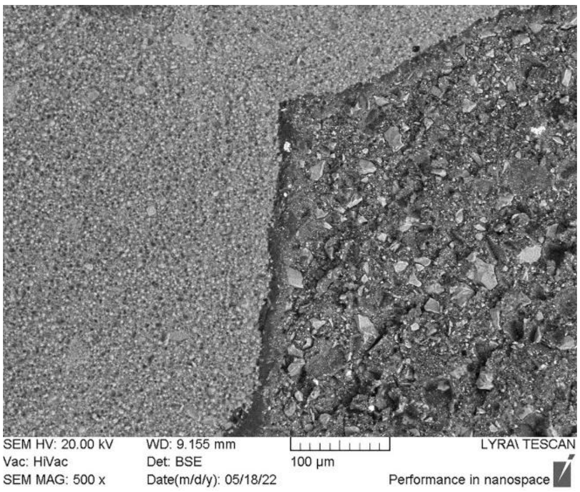

Fig. 4. Hybrid layer at TheraCal after postponed recovery 500^{x}

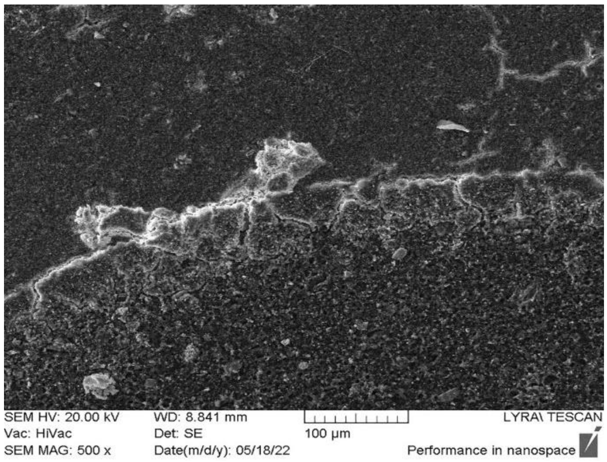

Fig. 5. Absence of hybrid layer at TheraCal after postponed recovery 500^{x}

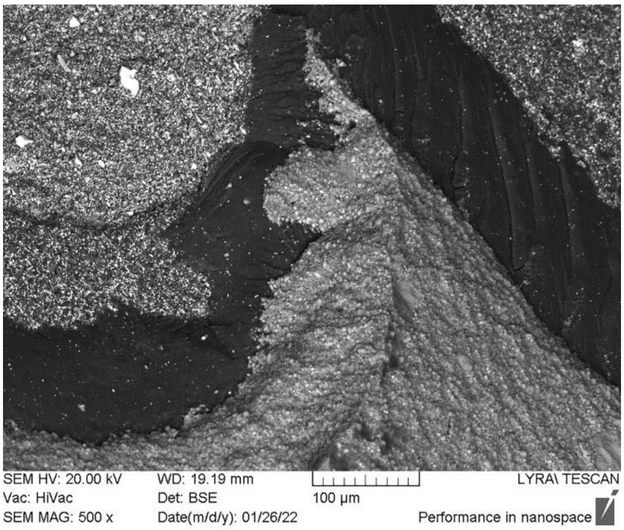

Fig. 6. Hybrid layer at TheraCal after immediate recovery 500^{x}

4. DISCUSSION

In the present study, only one type of CM and a universal adhesive system and protocol were used to compare the shear strength under the same standardized conditions, but at different time periods of recovery with a definitive filling material immediately after placement of the pulp capping agent and delayed placement for 2 weeks. In clinical practice, especially in cases of DPC it is particularly important to control the vitality of DP and therefore, it is necessary to postpone the final restoration for a certain proper time period. The goal was to establish the most favourable time period for restoration with a final restorative material to achieve and realize sufficient strength of the connection between the pulp capping agent and CM, a factor of extreme importance for the correct course of the healing process and durability of the restoration.

Most of the data in the literature regarding the proper time period of recovery with CM refer to Biodentine, but not to the hybrid ones [15, 23, 24, 25]. The question of the proper exact time to place CM over calcium-silicate cements has no unequivocal answer. There are no definite answers in the literature and the present information is contradictory. So, e.g. some authors found [26, 27] that delayed restoration for 7 or 14 days over Biodentine leads to an increase in the adhesive bond, but others found the exact opposite [28]. Therefore, a possible explanation is associated with the physicochemical properties of the various calcium-silicate cements.

Biomaterials that are used for DPC procedures should possess important properties such as biocompatible chemical composition to avoid adverse tissue reaction and pulp irritation, the ability to maintain pulp vitality, to adhere to dentine and the restorative material, and also to resist forces during restoration placement and function [22].

The chemical composition of the pulp capping materials studied in the present work represented a combination of components [5]. TheraCal LC contained bisphenol A-glycidyl methacrylate (5 – 20 %), hydroxyethyl methacrylate (HEMA) and urethane dimethacrylate monomers (10 – 50 %) [8]. These presented monomers had cytotoxicity which could affect a vital pulp [18]. In a study by Sanz et al. it was established that TheraCal LC exhibited significantly more cytotoxicity and reactive oxygen species production than Biodentine [3]. In our previous research through thermogravimetric analysis it was revealed that the new hybrid material BioCal-Cap was more resistant in comparison to TheraCal LC because no volatile compounds were found. The results after gas-chromatography of organic and inorganic and mass-spectrometry SIM mode analysis revealed that the extract of TheraCal LC contained nonreacted photoinitiators, while the same analysis for BioCal-Cap revealed no nonreacted monomers of HEMA [29]. Our data in this study was that the recovery with final restorative material was better delayed when using TheraCal in DPC, which was supported by finding on its certain cytotoxicity and the need for control on the vitality of DP.

To achieve a quality adhesive bond between CM and pulp capping agent there are important factors that need to be considered such as the type of light-curing resin adhesives, type of resin-based composites, type of resin modified cements [30].

ScotchBond Universal (3M ESPE, Monrovia, CA, USA) universal adhesive system was used. According to literature data, this adhesive system contains an acid monomer 10-methacrylolxidisyldehydrogen phosphate (10-MDP) with phosphate groups that form chemically stable salts with calcium but is inherently hydrophobic in which leads to a decrease in water absorption [31]. In the literature, there is conflicting information regarding the amount of calcium released from HCSC [18, 32]. According to Elbanna et al. [33] TheraCal LC showed a significant decreasing the release of Ca ions in a period of 14 days and drop after 28 days. But TheraCal LC had more bioactivity than the newly introduced TheraCal PT.

The lack of definitive data on calcium release from hybrid cements leaves open the question not only of the nature of the relationship between HCSC and CM, but also that of the biological potential of those materials.

And according to Pradelle [34] the composition of adhesive system with 10-MDP, led to the creation of a chemical bond and formed a layer with a homogeneous and correct structure.

Similar data have been reported by other authors [35]. And such a qualitative connection between different materials is a condition for resistance when absorbing and redistributing chewing stress [23].

The universal adhesive system can be used: as an etch-and-rinse or a self-etch mode, according to clinical conditions [36, 37]. Self-etch adhesives are attractive to practitioners since they can be used without the requirement for a rinse phase. As such, their use can significantly reduce application time. In the literature, however, there are conflicting data regarding the effect of the different protocol on the quality of the formed hybrid layer. Huan et al. found that the use of universal adhesives with the self-etch mode provides a stronger adhesive bond. Similar data have been reported by other authors [19, 20]. In contrast, Meraji et al. report that the etch-and-rinse technique is much more successful in creating a strong adhesive bond. It is more successful due to the modifications created by acid etching on the biomaterial surface [20, 21].

A large group of authors such as Sismanoglua et al. found no differences in the quality of the adhesive bond of the PPS under different clinical conditions and adhesive protocols [23]. According to Cengiz E et al. the use of a self-etching adhesives system increases the shear strength of Theracal LC [24]. In contrast, other authors Karadas et al. TheraCal LC found higher adhesive bond values between TheraCal LC total-etch adhesive system and universal composite resin Filtek Z250 [25].

According to Louis Hardan [26] higher values of shear strength of Theracal to CM were reported with the total-etch technique compared to self-etch using adhesive systems.

Data recorded in the literature regarding shear strength values of TheraCal LC are in a very wide range [25]. So e.g. Bhavika Jain and Dr. AmitaTiku described values of 8.805 Mpa between TheraCal LC and nanohybrid packable composite material 3M ESPE, Filtek Z350 XT and using an etch-and-rinse adhesive protocol. Similarly, low values of 6.544 between TheraCal LC and nanohybrid packable composite material 3M ESPE, Filtek Z350 XT and using an etch-and-rinse adhesive protocol were also found by other authors [21]. Karadas [38] reported different values for TheraCal LC when using different adhesive systems. Bond strength values TheraCal LC were significantly different among adhesives.

Cantekin [39] reported that the shear strength of Theracal to methacrylate CM is high and is within 19.3 MPa., which value is different and higher than that found by us. Close values of 12.84 MPa to our established values were reported by Alzraikat [20]. Our results for average TheraCal LC shear strength values of 16.35 MPa using self-etch mode on a universal adhesive system and Filtek Z350 were reported by Singla [40].

We found no data in the dental literature on the quality of the adhesive bond for the other hybrid tested CSC. In the present study, higher shear strength values were reported for Bio Cal-Cap at both time periods. So, e.g. reported values for immediate recovery for this material were 18.06 MPa versus 13.71 MPa for Theracal. The same trend was found for the delayed recovery with values of 20.25 MPa versus 15.58 MPa for TheraCal LC, respectively. The data clearly showed that the time of the composite material placement did not affect the shear bond strength in each of the observed groups, because in both of the tested materials there was no statistically significant difference in results after immediate and postponed placement of the composite material.

After analyses of the distribution of strength values for TheraCal more appropriate time for the composite material to be placed was two weeks after the setting of the pulp capping agent. In the new material BioCal-Cap there was the opposite tendency. Based on the results obtained from the present study, the second null hypothesis was rejected.

Analysis of the adhesive interface between the pulp-capping agent (PCA) and the composite material (CM) by scanning electron microscopy.

The selected post-destruction specimens were subjected to scanning electron microscopy to assess the hybrid layer between the PCA and CM. Its integrity was also a very important factor in the durability of the restoration. It also depends on the physicochemical characteristics of the biomaterial and the composite resin and the type of adhesive system that forms the adhesive interface a hybrid layer or interdiffusion zone between adhesive and CSC. As can be seen from the presented scanograms, this layer was homogeneous, properly structured, without the presence of microcracks and gaps, and had different thicknesses (Fig. 2 – Fig. 6). Only one sample of TheraCal was found to lack a hybrid layer (Fig. 5).

Similar to other studies, we found differences in the thickness of this layer depending on the time period of recovery of restoration. It was found that the thickness of this layer was significantly more pronounced in the group of samples that were restored immediately after the hardening of the PCA in both hybrid CSCs investigated in this study. Similar data on variations in the thickness of this hybrid layer have been found by other authors [41, 42, 43].

5. CONCLUSIONS

It was found that the new hybrid CSC BioCal-Cap provided higher values of shear strength compared to Theracal, although the obtained differences between them were not statistically significant. These reported shear bond strength values for the new hybrid cement indicated, that it could resist masticatory stress during function.

The data from this study clearly showed that the time of the composite material placement did not affect the shear bond strength in each of the observed groups. The median value was shifted higher after immediate composite placement, which supported a one-step treatment approach at the novel hybrid material BioCal-Cap. For the TheraCal LC, there was the opposite tendency. It was reported that the thickness of the hybrid layer was significantly more pronounced in the group of samples that were restored immediately after the hardening
Of the PCA.

REFERENCES

1. **Suh, B., Yin, R., Cannon, M., Martin, D.** Polymerizable Dental Pulp Healing, Capping and Lining Material and Method for Use. Google patent US20080318190 A1. 2008.
2. **Dammaschke. T.** The History of Direct Pulp Capping *Journal of History of Dentistry* 56 (1) 2008: pp. 9 – 23.
3. **Sanz, J.L., Soler-Doria, A., Lopez-García, S., García-Bernal, D. Rodríguez-Lozano FJ, Lozano A, Llena C, Forner L, Guerrero-Gironés J, Melo M.** Comparative Biological Properties and Mineralization Potential of 3 Endodontic Materials for Vital Pulp Therapy: Theracal Pt, Theracal Lc, and Biodentine on Human Dental Pulp Stem Cells *Journal of Endodontics* 47 2021: pp. 1896 – 1906. https://doi.org/10.1016/ j.joen.2021.08.001
4. **Nour, S., Baheiraei, N., Imani, R., Navid, R., Khodaei, M., Alizadeh, A., Seyed, M.M.** Bioactive Materials: A Comprehensive Review on Interactions with Biological Microenvironment Based on the Immune Response *Journal of Bionic Engineering* 16 2019: pp. 563 – 581. https://doi.org/10.1007/s42235-019-0046-z
5. **Minet, J., Abramson, S., Bresson, B., Franceschini, A., Van Dammea, H., Lequeux, N.** Organic Calcium Silicate Hydrate Hybrids: A New Approach to Cement Based Nanocomposite *Journal of Materials Chemistry* 16 (14) 2006: pp. 1379 – 1383.https://doi.org/10.1039/B515947D
6. Bisco, Schamurg, IL, USA. https://www.bisco.com/theracal-lc-/
7. Harvard Dental International, Germany. https://harvard-dental-international.de/en/products/endodontics/cap-pulp-protection/harvard-biocal-cap/
8. **Arandi, N.Z., Rabi, T.** Theracal Lc: from Biochemical and Bioactive Properties to Clinical Applications *International Journal of Dentistry* ID3484653 2018: p. 6. https://doi.org/10.1155/2018/3484653
9. **Santos, J.M., Pereira, J.F., Marques, A., Sequeira, D.B., Friedman, S.** Vital Pulp Therapy in Permanent Mature Posterior Teeth with Symptomatic Irreversible Pulpitis: A Systematic Review of Treatment Outcomes *Medicina* 57 (573) 2021: pp. 2 – 14. https://doi.org/10.3390/medicina57060573
10. **Peskersoy, C., Lukarcanin, J., Turkun, M.** Efficacy of Different Calcium Silicate Materials as Pulp Capping Agents: Randomized Clinical Trial *Journal of Dental Sciences* 16 2021: pp. 723 – 731. https://doi.org/10.1016/j.jds.2020.08.016
11. **Alqahtani, A.R, Yaman, P., McDonald, N., Dennison, J.** Efficacy of Calcium Hydroxide and Resin-Modifyed Calcium Silicate as Pulp-Capping Materials; A Retrospective Study *General Dentistry* 2020: pp. 50 – 54.
12. **Tyagi, N., Chaman, C., Tyagi, S.P., Singh, U.P., Sharma, A.** The Shear Bond Strength of MTA eith Three Different Types of Adhesive Systems: An in Vitro Study *Journal Conservative Dentistry* 19 2016: pp. 130 – 133.
13. **Hikita, K., Van Meerbeek, B., De Munck, J., Ikeda, T., Van Landuyt K., Maida, T., Lambrechts, P., Peumans, M.** Bonding Effectiveness of Adhesive Luting Agents to Enamel and Dentin *Dental Materials* 23 2007: pp. 71 – 80. https://doi.org/10.1016/j.dental.2005.12.002
14. **Takamizawa, T., Barkmeier, W.W., Tsujimoto, A., Endo, H., Tsuchiya, K., Erickson, R.L., Latta, M.A., Miyazaki, M.** Influence of Pre-Etching Times on Fatigue Strength of Sel-Etch Adhesives to Enamel *Journal Adhesive Dentistry* 18 (6) 2016: pp. 501 – 511. https://doi.org/10.3290/j.jad.a37361
15. **Çolak, H., Tokay, U., Uzgur, R., Uzgur, Z. Ercan, E., Hamidi, M.M.** The Effect of Different Adhesives and Setting Times on Bond Strength Between Biodentine and Composite *Journal of Applied Biomaterials & Functional Materials* 14 (2) 2016: pp. e217 – e222. https://doi.org/ 10.5301/jabfm.5000266
16. **Sismanoglua, S., Yildirim-Bilmezb, Z., Gurcanc, A.T., Gumustasd, B.** Influence of Application Mode of Universal

Adhesive on the Surface Morphology Elemental Composition and Bond Strength of Calcium Silicate-based Cements to Composite Resin: A Sem-Edx Microanalysis Study *Journal of Adhesion Science and Technology* 2021: pp. 513 – 519. https://doi.org/10.1080/01694243.2021.1992979

17. **Cengiz, E, Ulusoy, N.** Microshear Bond Strength of Tri-Calcium Silicate-Based Cements to Different Restorative Materials *Journal of Adhesive Dentistry* 18 (3) 2016: pp. 231 – 237. https://doi.org/10.3290/jad.a35934
18. **Gandolfi, M.G., Siboni, F., Prati, C.** Chemical-physical Properties of Theracal, A Novel Ligth-curable Mta-like Material for Pulp Capping *International Endodontic Journal* 45 2012: pp. 571 – 579. https://doi.org/ 10.1111/j.1365-2591.2012.02013.x
19. **Van Meerbeek, B., Peumans, M., Poitevin, A., Mine, A., Van Ende, A., Neves, A., De Munck, J.** Relationship Between Bond-Strength Tests and Clinical Outcomes *Dental Materials* 26 2010: pp. e100 – e121. https://doi.org/ 10.1016/j.dental.2009.11.148
20. **Alzraikat, H., Tana, N.A., Qasrawi, D., Burrow, M.F.** Shear Bond Strength of a Novel Light Cured Calcium Silicate Based-cement to Resin Composite Using Different Adhesive Systems *Dental Materials Journal* 35 (6) 2016: pp. 881 – 887. https://doi.org/ 10.4012/dmj.2016-075
21. **Boby, A., Pai, D., Ginjupalli, K., Gaur, S.** Comparison of Shear Bond Strength of Light Cure Mineral Trioxide Aggregate and Light Cure Calcium Hydroxide with Nanofilled Composite: A Stereomicroscopic and Scanning Electron Microscope Analysis *Journal of the Indian Society of Pedodontics and Preventive Dentistry* 38 2020: pp. 56 – 63. https://doi.org/ 10.4103/JISPPD.JISPPD_178_19
22. **Hardan, L., Mancino, D., Bourgi, R., Alvarado-Orozco, A., Rodríguez-Vilchis, L.E., Flores-Ledesma, A., Cuevas-Suárez, C.E., Lukomska-Szymanska, M., Eid, A., Danhache, M.L., Minoux, M., Haïkel, Y., Kharouf, N.** Bond Strength of Adhesive Systems to Calcium Silicate-based Materials: A Systematic Review and Meta-analysis of in Vitro Studies *Gels* 8 (311) 2022: pp. 2 – 18. https://doi.org/10.3390/gels8050311
23. **Altunsoy, M., Tanriver, M., Ok, E., Kucukylmaz, E.** Shear Bond Strength of a Self-adhering Flowable Composite and a Flowable Base Composite to Mineral Trioxide Aggregate, Calcium-Enriched Mixture Cement, and Biodentine *Journal of Endodontics* 41 2015: 1691 – 1695. https://doi.org/10.1016/j.joen.2015.06.013
24. **Krawczyk-Stuss, M., Nowak, J., Bołtacz-Rzepkowska, E.** Bond Strength of Biodentine to a Resin-based Composite at Various Acid Etching Times and with Different Adhesive Strategies *Dental and Medical Problem* 56 (1) 2019: pp. 39 – 44. https://doi.org/ 10.17219/dmp/103589
25. **Bhavika, J., Tiku, A.** A Comparative Evaluation of Shear Bond Strength of Three Different Restorative Materials to Biodentine and Theracal LC: An in Vitro Study *International Journal of Applied Dental Sciences* 5 (2) 2019: pp. 426 – 429.
26. **Odabaş, M.E., Bani, M., Tirali, R.E.** Shear Bond Strength of Different Adhesive Systems to Biodentine *Scientific World Journal* 62 (6) 2013: pp. 61 – 65. https://doi.org/10.1155/2013/626103
27. **HoangThai, Ha.** The Effect of the Maturation Time of Calcium Silicate-based Cement (Biodentine) on Resin Bonding; An in Vitro Study *Applied Adhesion Science* 7 (1) 2019: pp. 2 – 13. https://doi.org/10.1186/s40563-019-0118-7
28. **Palma, P.J., Marques, J.A., Falacho, R.I., Vinagre, A., Santos, J.M., Ramos, J.C.** Does Delayed Restoration Improve Shear Bond Strength of Different Restorative Protocols to Calcium-silicate Cements? *Materials* 11 (2216) 2018: pp. 2 – 10. http://dx.doi.org/10.3390/ma11112216
29. **Tsanova-Tosheva, D., Dimitrova, I., Kouzmanova, Y.** 3analysis of the Organic Content in Two Hybrid Calcium-silicate Cements *International Conference Proceeding Series* 2022: pp. 1 – 6. https://doi.org/10.1145/3502060.3502276
30. **Munksgaard, E.C., Peutzfeldt, A., Asmussen, E.** Elution of Tegdma and Bisgma from a Resin and Resin Composite Cured with Halogen or Plasma Ligth *European Journal of Oral Sciences* 108 2000: pp. 341 – 345. https://doi.org/10.1034/j.1600-0722.2000.108004341.x
31. **Ghajari, M.F., Ghasemi, A., Badiee, M., Abdolazimi, Z., Baghban, A.** Microshear Bond Strength of Scotchbond Universal Adhesive to Primary and Permanent Dentin: A Six Month in Vitro Study *Frontiers in Dentistry* 16(3) 2019: 173 – 180. https://doi.org/10.18502/fid.v16i3.1587
32. **Camilleri, J.** Hydration Characteristics of Biodentine and Theracal Used as Pulp Capping Materials *Dental Materials* 30 2014: pp. 709 – 715. https://doi.org/10.1016/j.dental.2014.03.012
33. **Elbanna, A., Atta, D., Sherief, D.I.** In Vitro Bioactivity of Newly Introduced Dual Resin-Modified Calcium Silicate Cement *Dental Research Journal* 19 2022: pp. 1 – 11. https://doi.org 10.4103/1735-3327.336686
34. **Pradelle-Plasse, N., Mocquot, C., Semennikova, K., Colon, P., Grosgogeat, B.** Interface Between Calcium Silicate Cement and Adhesive Systems According to Adhesive Families and Cement Maturation *Restorative Dentistry and Endodontics* 46 (1) 2021: pp. 1 – 14. https://doi.org/ 10.5395/rde.2021.46.e3
35. **Yoshida, Y., Nagakane, K., Fukuda, R., Nakayama, Y., Okazaki, M., Shintani, H.,** Inoue S, Tagawa Y, Suzuki K, De Munck J, Van Meerbeek B.Comparative Study on Adhesive Performance of Functional Monomers *Journal Dental Research* 83 (6) 2004: pp. 454 – 458. https://doi.org/10.1177/154405910408300604
36. **Hanabusa, M., Mine, A., Kuboki, T., Momoi, Y., Van Ende, A., Van Meerbeek, B., De Munck, J.** Bonding Effectiveness of a New 'Multi-Mode'adhesive to Enamel and Dentine *Journal Dentistry* 40 2012: pp. 475 – 484. https://doi.org/10.1016/j.jdent.2012.02.012
37. **Ragab, H., Zyara, Y., Osman, E.** Influence of Etching Aggressiveness of Universal Adhesives on Longevity of Resin Dentin Bonding Using Self Etch *Egyptian Dental Journal* 64 (2) 2018: pp. 1915 – 1924. https://dx.doi.org/10.21608/edj.2018.78451
38. **Karadas, M., Cantekin, K., Gumus, H. Atess, S.M., Duymuss, Z.Y.** Evaluation of the Bond Strength of Different Adhesive Agents to a Resin-modified Calcium Silicate Material (Theracal LC) *Scanning* 9999 2015: pp. 1 – 9. https://doi.org/10.1002/sca.21284
39. **Cantekin, K.** Bond Strength of Different Restorative Materials to Light-curable Mineral Trioxide Aggregate *Journal of Clinical Pediatric Dentistry* 39 2015: pp. 143 – 148. https://doi.org/10.17796/jcpd.39.2.84x57tp110k46183

40. **Singla, M.G., Wahi, P.** Comparative Evaluation of Shear Bond Strength of Biodentine, Endocem Mineral Trioxide Aggregate, and Theracal LC to Resin Composite Using a Universal Adhesive: An in Vitro Study *Endodontology* 32 2020: pp. 14 – 19. https://doi.org/10.4103/endo.endo_7_199

41. **Van Meerbeek, B., Peumans, M., Poitevin, A., Mine, A., Van Ende, A., Neves, A., De Munck, J.** Relationship Between Bond-Strength Tests and Clinical Outcomes *Dental Materials* 26 2010: pp. e100 – 121. https://doi.org/ 10.1016/j.dental.2009.11.148

42. **Xavier, M.T., Ana Luísa Costa, A.L., Caramelo, F.J., Palma, P.J., Ramos, J.C.** Evaluation of the Interfaces Between of Restorative and Regenerative Biomaterials Used in Vital Pulp Therapy *Materials* 14 (5055) 2021: pp. 2 – 21. https://doi.org/10.3390/ma14175055

43. **Marchesi, G., Frassetto, A., Mazzoni, A., Apolonio, F., Diolosà, M., Cadenaro, M., Di Lenarda, R., Pashley, D.H., Tay, F., Breschi, L.** Adhesive Performance of a Multi-Mode Adhesive System: 1-year in Vitro Study *Journal Dentistry* 42 (5) 2014: pp. 603 – 612. https://doi.org/10.1016/j.jdent.2013.12.008