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Evaluation of adhesive interfaces calcium silicate cements/composite resin: An in vitro study

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Abstract

Aim: The aim of the present *in vitro* study was to evaluate the shear bond strength inherent to immediate and delayed definitive composite resin restorations, over three different biomaterials using a two-step self-etch adhesive system.

Materials and Methods: A total of 54 metallic blocks (30mm height x 15mm diameter) were produced containing a central cavity measuring 4mm diameter and 2mm height. The blocks were randomly assigned to six experimental groups (n=9) according to the three biomaterials and the two restoration times evaluated. Specimens from the immediate groups were filled with Biodentine (group 1), TotalFill putty (group 3) and PulpGuard (group 5). After air-drying the biomaterial surface, a two-step self-etch bonding system (Clearfil™ SE Bond) was applied according to the manufacturer's instructions, except for the active application which was not performed, and subsequently "restored" using a flowable composite resin cylinder (SDR™). For the delayed groups (group 2 – Biodentine; group 4 – TotalFill putty; and group 6 - PulpGuard), the samples were filled with the capping biomaterials one week prior to the adhesive/restorative procedures. All samples were stored in an incubator at 37ºC with 100% humidity for 48 hours before proceeding the shear bond strength tests in an universal testing machine. Data analyses was performed using an ANOVA test (p<0,05).

Results: Concerning the capping biomaterial, within the immediate groups, Biodentine showed the highest mean shear bond strength value, although not statistically different (p>0,05) to TotalFill putty and PulpGuard groups. Regarding the 7-days groups, group 2 (Biodentine) and group 4 (TotalFill putty) presented higher mean shear bond strength values, with statistically significant differences (p<0,05) compared with group 6 (PulpGuard). Concerning the timing of the adhesive/restorative procedures there were no statistically significant differences (p>0,05) between immediate and delayed groups for all the 3 materials.

Discussion and Conclusions: Within the limitations of this in vitro study, Biodentine and TotalFill putty have shown superior shear bond strength results when compared with PulpGuard, within delayed restorations (7-days). Our findings suggest that Biodentine allows restorative procedures immediately after pulp-capping biomaterial placement (12 minutes), requiring one single appointment to complete the procedure.

Key words: Biodentine, calcium silicate cements, composite resin restorations, flowable composite resin, PulpGuard, regenerative endodontics procedures, self-etch adhesive, shear bond strength, Totalfill BC putty, vital pulp therapy.

Resumo

Objetivo: Avaliar as forças de adesão inerentes a restaurações adesivas em resina composta realizadas imediatamente ou uma semana após a aplicação de 3 biomateriais usados em tratamentos pulpares conservadores, com recurso a um sistema adesivo auto-condicionante de 2 passos.

Materiais e Métodos: Um total de 54 blocos metálicos foram fabricados (30mm altura x 15mm diâmetro) contendo um halo central vazio com 4mm de diâmetro e 2mm de altura. Os blocos foram aleatoriamente distribuídos em 6 grupos experimentais (n=9) de acordo com os três biomateriais e os dois tempos de restauração avaliados. As amostras dos grupos de restauração imediata foram preenchidas com Biodentine (grupo 1), TotalFill putty (grupo 3) e PulpGuard (grupo 5). Depois da presa inicial dos biomateriais (3 ou 12 minutos), foi aplicado de forma não ativa o sistema adesivo auto-condicionante de 2 passos (Clearfil™ SE Bond) sobre o qual foi efetuada uma restauração cilíndrica em resina composta fluida (SDR™). Para os grupos dos 7 dias (grupo 2 – Biodentine; grupo 4 – TotalFill putty; e grupo 6 - PulpGuard), após o preenchimento dos halos com o biomaterial, as amostras foram armazenadas numa incubadora a 37ºC com 100% de humidade durante uma semana antes da realização dos procedimentos restauradores efetuados tal como nos grupos de restauração imediata. Todas as amostras foram colocadas numa incubadora a 37ºC com 100% de humidade, previamente aos testes de adesão realizados com uma máquina de testes universal. A análise estatística foi realizada com o teste ANOVA ($p<0,05$).

Resultados: No que se refere ao efeito do biomaterial, considerando os grupos de restauração imediata, o grupo 1 (Biodentine) apresentou valores de força de adesão mais elevados, no entanto sem diferenças estatisticamente significativas ($p>0,05$) com os grupos 3 (TotalFill putty) e 5 (PulpGuard). Considerando os grupos de restauração aos 7 dias, o grupo 2 (Biodentine) e o grupo 4 (TotalFill) apresentaram a média dos valores de força de adesão estatisticamente mais elevada ($p<0,05$) quando comparado com o grupo 6 (PulpGuard). No que se refere ao efeito do tempo de restauração, não se verificaram diferenças estatisticamente significativas entre os grupos imediatos e diferidos para quaisquer dos 3 biomateriais.

Discussão e Conclusão: Considerando as limitações deste estudo *in vitro*, o Biodentine e o TotatlFill BC putty mostraram resultados superiores de forças de adesão quando comparados com o PulpGuard, nas restaurações diferidas (aos 7 dias). Os resultados sugerem que o Biodentine pode permitir a restauração adesiva imediata (12 minutos após a sua colocação), possibilitando a realização de todo o procedimento numa única sessão.

Palavras-chave: Biodentine, cimentos de silicato de cálcio, restaurações com resina composta, compósito fluido, PulpGuard, procedimentos endodônticos regenerativos, sistema adesivo self-etch, força de adesão, TotalFill BC putty, tratamentos de polpa vital

Introduction

Aiming to maintain pulp vitality and health after traumatic injuries or carious exposure, vital pulp therapy (VPT) has gained increasing interest in dentistry.[1] VPT approaches include both direct/indirect pulp capping and pulpotomy procedures.[1,2] Although VPT has been reported as a promising approach in asymptomatic and immature teeth, it nowadays encompasses a diverse range of clinical situations, as spontaneous and severe pain does not necessarily present an inability of the pulp to repair.[3,4] Available literature refers that biomaterials improvement led to a higher success rate of pulpotomy procedures in cases of permanent teeth with irreversible pulpitis, rather than the classical root canal treatment, where the ability to control bleeding is crucial for a successful outcome.[5,6] Calcium hydroxide was formerly the most widely used material for these procedures.[5,6] However it has been reported that $Ca(OH)_2$ dissolves overtime, does not adhere to the dentin and may promote the creation of multiple tunnel defects in dentin bridges adjacent to the biomaterial.[7] Bioactive cements, such as hydraulic calcium silicate-based cements (HCSCs), have recently been introduced as alternative materials.[5]

The first HCSC developed for endodontic treatments was the mineral trioxide aggregate (MTA).[8] MTA emerged in the field of dentistry in 1993, exhibiting tricalcium aluminate, tricalcium silicate, dicalcium silicate, tetracalcium aluminoferrite, and bismuth oxide within its composition.[7] MTA was originally developed as a root-end filling material.[9] Currently its range of clinical applications also includes pulp capping procedures, apexogenesis, pulpotomy, repair of root perforations and internal/external resorptions, root canal filling and apical barrier formation (apexification) in immature permanent teeth with pulp necrosis.[9] This bioceramic material shows several clinical and biological advantages such as low solubility, biocompatibility, bioactivity, prevention of bacterial leakage, ability to release calcium hydroxide (antibacterial activity)[1] and to set in a wet environment, even in the presence of blood.[7,10] Nevertheless, it has some well-described shortcomings including long setting time, difficulty in handling and discoloration potential of dental tissue.[7,9,11] In order to overcome the MTA undesirable proprieties, second-generation tricalcium silicate-based materials were introduced, such as Biodentine.[12]

Biodentine is a water-based cement presented as a powder in a capsule, composed of tricalcium silicate, calcium carbonate, and zirconium oxide, and a liquid containing calcium chloride and a water-reducing agent. [7,11,12] This bioactive cement presents itself as a dentin replacement material.[12] Its physical properties comprise greater sealing ability and high compressive strength [13,14] ,and its biological characteristics include bioactivity, biocompatibility and biomineralization capacity.[15,16] The main advantages of Biodentine over MTA are its shorter setting time, of approximately 12 minutes[7,12], its superior color stability[17] and higher viscosity.[7]

In 2006, a new generation of biological cements, the calcium phosphate silicate cements (CPSCs), was proposed. In addition to hydraulic calcium silicates cements, CPSC also contain phosphate salts. These sealers were developed based on the principle that the hydration process would improve their biological and mechanical properties.[8,18] EndoSequence Root Repair Material Paste (ERRM Paste; Brasseler, USA) and EndoSequence Root Repair Material Putty (ERRM Putty; Brasseler

USA, Savannah, GA, USA) are examples of CPSC.[8] ERRM Putty is marketed as a root repair material and it can be used for resorption and perforation repair, retrograde filling, root-end closure and pulp capping procedures.[19] According to the manufacturer, ERRM is composed of calcium silicates, calcium phosphate monobasic, zirconium oxide, tantalum oxide and filler agents.[20] Concerning TotalFill® BC RRM™ putty (FKG, La Chaux-de-Fonds, Switzerland) Zamparini *et al.* research suggests a fast setting time of 2 hours.[18] Nevertheless, the long setting time of HCSCs and CPSCs is one of the potential downsides of these materials, which therefore may require more than one appointment to complete the treatment.[8]

Recently, a new bioactive cement named PulpGuard (Coltène/Whaledent, Altstätten, Switzerland) has been developed. This new biomaterial shares the clinical applications of both Biodentine and MTA.[21] Its formula comprises silicates, polydimethylsiloxane, silicon oils, platinum catalyst, zinc oxide, zirconium dioxide, bioactive glass and pigment.[21] Despite the presence of the ion Zn^{2+} within its composition, recently published data shows a good cytocompatibility with human cells from the apical papilla.[21] Preliminary data shared by the manufacturer indicate a record setting time of approximately 3 minutes for PupGuard biomaterial confirmed in a recent study.[21]

It is important to highlight that an exposed pulp can repair itself and form a dentinal bridge when sterile environment is guaranteed, otherwise the presence of bacteria may induce pulp response, ultimately leading to pulp necrosis.[22] Therefore, an adequate bond between the restorative material and the pulp capping agent is crucial to ensure a proper seal and avoid clinical failure.[1,2,22–24] Besides the clear biological benefit, it would be clinically desirable for both clinicians and patients if the permanent restorations could be placed over the bioceramic material during the same appointment, thus reducing costs and time.[1] However, the literature remains unclear concerning the restorative protocol to perform after pulp capping material placement,[7,12] as well as the preferable timing for the permanent restoration.[1,25]

The aim of the present *in vitro* study was to evaluate the shear bond strength inherent to immediate and delayed definitive composite resin restorations, over three different biomaterials (Biodentine™, TotalFill® BC RRM™ putty and PulpGuard), using a two-step self-etch adhesive system.

The tested null hypothesis declares that there are no significant differences between the different materials and timings of restoration evaluated concerning shear bond strength values.

Materials and Methods

The materials used in the present study are shown in table 1.

Table 1 – Manufacturer, composition, steps for application, lot number and expiration date details of the materials used in the study.

Material	Manufacturer	Composition	Steps for application	Lot number	Expiration date
Biodentine™ Bioactive dentin substitute	Septodont, Saint-Maur des-Fossés Cedex, France	Powder: tricalcium silicate, zirconium oxide, calcium oxide, calcium carbonate and colourings Aqueous solution: calcium chloride and polycarboxylate	1.Pour 5 drops of liquid into the capsule 2.Place the capsule on a mixing device 3.Mix for 30 seconds	B21183	06-2019
TotalFill® BC RRM™ putty Tricalcium silicate material	FKG, La Chaux-de-Fonds, Switzerland	Zirconium oxide, calcium silicates, tantalum pentoxide, calcium phosphate monobasic, filler agents	1.Ready to apply	1702BPP	11-2019
PulpGuard Bioactive cement	Coltène/Whaledent, Altstätten, Switzerland	Silicates, polydimethylsiloxane, silicon oils, platinum catalyst, zinc oxide, zirconium dioxide, bioactive glass and pigment	1.Apply with auto-mixing tips	2018120-P3-RR	08-2019
Clearfil™ SE Bond Two step Self-etch adhesive system	Kuraray Noritake, Tokyo, Japan	Primer: MDP, HEMA, dimethacrylate monomer, water, photoinitiator Bond: MDP, HEMA, dimethacrylate monomer, microfiller, photoinitiator	1.Apply primer and leave for 20 seconds and dry with mild air flow 2.Apply bond and distribute evenly with mild air flow 3.Light cure for 10 seconds	Primer 4Q0068 Bond 5P0102	07-2020 08-2020
SDR™ Bulk-fill flowable composite	Dentsply DeTrey GmbH, Konstanz, Germany	Barium-alumino-luoroborosilicate glass, strontium alumino- fluoro-silicate glass, modified urethane dimethacrylate resin, EBPADMA, TEGDMA, CQ, photoaccelerator, BHT, UV stabilizer, titanium dioxide, iron oxide pigments, fluorescing agent	1.Dispense SDR™ material 2.Light-curing for at least 20 seconds	02023	02-2020

Specimen preparation

A total of 54 metallic blocks (30mm height x 15mm diameter) were produced containing a central cavity measuring 4mm diameter and 2mm height. The blocks were randomly divided in six experimental groups (n=9) according to the three biomaterials and the two restoration times evaluated (Table 2). The number of samples included in the present study are based on a previous sample size calculation, performed in G*Power software. The metallic blocks were specifically designed and fabricated by the Laboratory of Applied Biomechanics of the Engineering Institute of Polytechnic Institute of Coimbra (Department of Mechanical Engineering) to be used in the present *in vitro* study.

Table 2 – Details of the experimental groups, with restauration timing, bioactive cement, bonding system and restorative material.

Group	Experimental group	Restoration timing	Bioactive cement	Bonding system	"Restorative" material
1	Biodentine 12-min	12-minutes	Biodentine™	Clearfil™ SE Bond	SDR™
2	Biodentine 7-days	7-days			
3	TotalFill putty 12-min	12-minutes	TotalFill® BC RRM™ putty	Clearfil™ SE bond	SDR™
4	TotalFillputty 7-days	7- days			
5	PulpGuard 3-min	3-minutes	PulpGuard	Clearfil™ SE Bond	SDR™
6	PulpGuard 7-days	7-days			

Biomaterial placement

Specimens for the immediate groups were filled with Biodentine (group 1), TotalFill putty (group 3) and PulpGuard (group 5). Bioceramic materials were prepared according to the manufacturer's instructions (table 1) and placed in the metallic blocks using a spatula.

For the 7 days groups, one week prior to the shear bond strength test, the three groups were filled with either Biodentine™ (group 2) TotalFill® BC RRMTM putty (group 4) or PulpGuard (group 6). Biomaterials were prepared and placed likewise in groups 1, 3 and 5. Samples were stored in an incubator at 37ºC with 100% of humidity for one week for total setting before restorative procedures.

During all specimen preparation, the room temperature was 23,8ºC with 40% humidity and the biomaterial placement was performed under a dental microscope (Leica M320, Leica Microsystems, Heerbrugg Switzerland) at 16x magnification, with the metallic blocks on top of a vibrating base to obtain a uniform regular surface and a biomaterial layer free of voids.

Restorative procedure

For the immediate groups (group 1, 3 and 5), after initial setting (12 minutes for Biodentine and TotalFill; 3 minutes for PulpGuard) the sample's surface was air-dried and a two-step self-etch bonding system (Clearfil™ SE Bond, Kuraray Medical, Okayama, Japan) was applied according to the manufacturer's instructions, except for the active application which was not performed.

For the delayed restoration groups (group 2, 4 and 6), after 7-days of storage, the biomaterial surface was polished with an abrasive sandpaper P1000 (WS-FLEX 18-C, HERMES, Hamburg, Germany), prior to the restorative procedures. Subsequently, the same two-step self-etch bonding system was applied over the capping materials according to the manufacturer's instructions (table 1), with active application of both primer and bond being performed for 20 seconds. After adhesive photopolymerization (10 seconds), the "restorative" material (SDR TM flowable composite) was centrally placed over the capping material in all samples using cylindrical capsules with 4,39mm height and 2,54mm of internal diameter and light cured with a polywave LED curing light source (Bluephase® Style M, Ivoclar, Vivadent,Schaan,Liechtenstein) for 80 seconds (20 seconds/quadrant).

All 54 samples were stored in an incubator at 37ºC with 100% humidity for 48 hours, before proceeding to the shear bond strength tests.

Shear bond strength (SBS) test

For the adhesive tests, each block was secured in a universal test machine (Model AG-I, Shimadzu Corporation, Kyoto, Japan), in a shear mode (Figure 1). The force was applied at a crosshead speed of 0,5mm/min with a chisel-shaped rod. The force necessary to remove the restorative material from the pulp capping material was measured in Newtons (N). The shear-bond values, calculated by the quotient between the peak break force (N) and the adhesion interface area (5,07 mm^2), are expressed in MegaPascals (MPa) (1MPa = 1 N/mm^2).

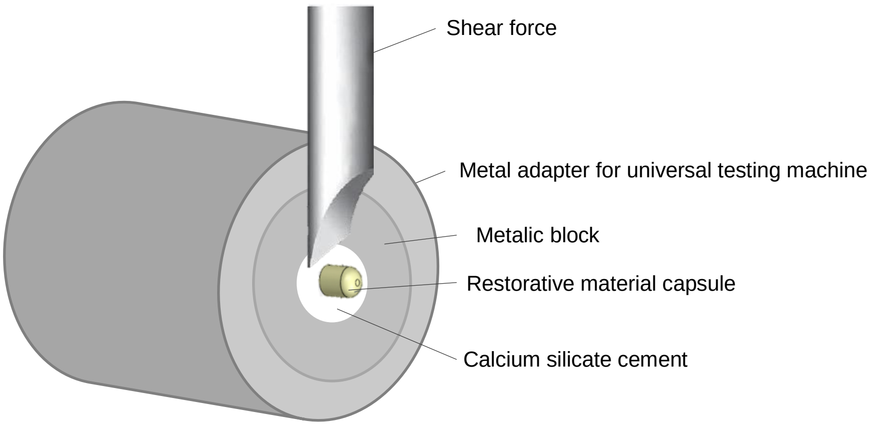

Figure 1 – Schematic illustration of shear bond strength test (Adapted from Palma *et al.*[26]).

Fracture analysis

The fracture surfaces were evaluated by a single operator under a dental microscope (Leica CLS 150 MR) with 40x magnification. The fracture pattern was classified as follows: adhesive fracture, cohesive fracture in the biomaterial, cohesive fracture in the restorative material or mixed fracture.

Statistical analysis

All calculations were performed using statistical software, (IBM SPSS version 24, Chicago, IL, USA), with a significant level of $p<0{,}05$. The shear bond strength results were described within mean, standard deviation, minimum and maximum values. The distribution of this values was accomplished by a box-plot analysis. In order to testify the normality of data distribution was used the Shapiro-Wilk test. Attending to the normal distribution of data, the ANOVA test was carried out, aiming to show the existence of statistically significant differences between the median across the groups. Post-hoc comparison between the groups were performed using Turkey tests. The association between the fracture type and the biomaterial was performed using Fisher's exact test. The shear bond strength values were expressed in MPa.

Results

For this experimental study, the results were showed in Table 3 and Figure 2.

Table 3 – Mean, standard deviation, minimum and maximum values of shear bond strength (MPa) of the tested groups.

		N	**Mean** (MPa)	**Standard deviation**	**Minimum**	**Maximum**
Group	1- Biodentine 12 min	9	5.49	4.28	0.96	13.01
	2- Biodentine 7days	9	6.98	4.51	2.35	15.57
	3- TotalFill putty 12 min	9	1.22	0.60	0.25	2.08
	4- TotalFill putty 7 days	9	5.22	4.56	1.62	15.88
	5- PulpGuard 3 min	9	2.07	0.83	0.47	3.09
	6- PulpGuard 7 days	9	0.49	0.37	0.03	1.22

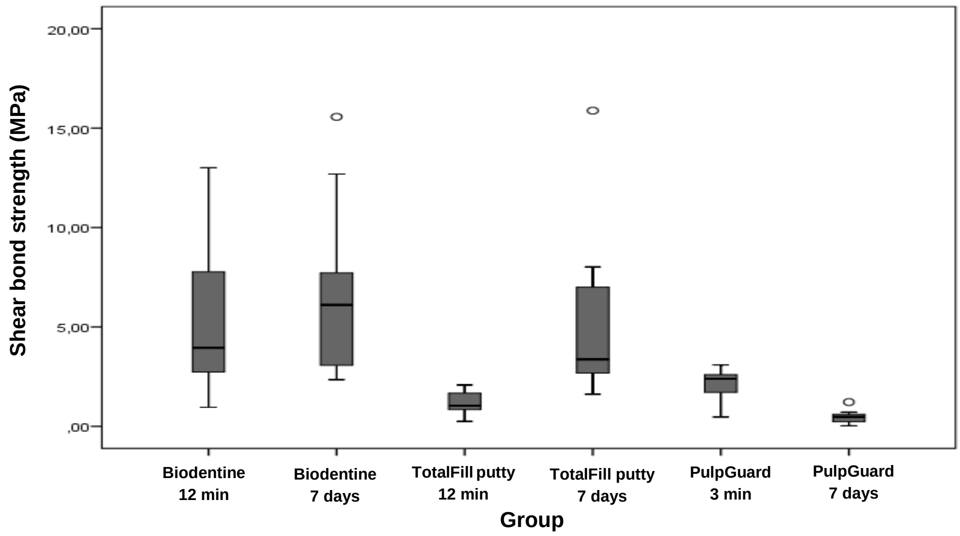

Figure 2 – Box-plot of shear bond strength values distribution in the tested groups.

Table 4 – Comparison *p* values of the tested groups (* - represented statistically significant differences).

Group	Biodentine 7days	TotalFill putty 12 min	TotalFill putty 7 days	PulpGuard 3 min	PulpGuard 7 days
Biodentine 12 min	0.920	0.072	1.000	0.232	**0.028***
Biodentine 7days		**0.005 ***	0.853	**0.025***	**0.002***
TotalFill putty 12 min			0.108	0.993	0.997
TotalFill putty 7 days				0.314	**0.043***
PulpGuard 3 min					0.912

There are statistically significant differences ($\chi^2(5,47) = 5.966$; $p<0.001$) concerning the shear bond strength in the tested groups (Table 3 and Figure 2).

Within the immediate groups, Biodentine (group 1) showed the highest mean shear bond strength value, with no statistically significant differences (*p*>0,05) compared with both TotalFill putty (group 3) and PulpGuard (group 5) groups (Table 4).

Regarding the 7-days groups, Biodentine (group 2) and TotalFill putty (group 4) presented the highest mean shear bond strength value (Table 3 and Figure 2), with statistically significant differences (*p*<0,05) when compared with 7-days PulpGuard (group 6) group (Table 4).

Concerning the three biomaterials (Biodentine, TotalFill putty and PulpGuard), there were no statistically significant differences (*p*>0,05) between both immediate and delayed groups.

Table 5 – Fracture modes of the tested groups after shear bond strength tests.

Fracture	Biodentine 12 min	Biodentine 7days	TotalFill putty 12 min	TotalFill putty 7 days	PulpGuard 3 min	PulpGuard 7 days
Adhesive	6	6	1	0	9	9
Cohesive within biomaterial	2	2	8	5	0	0
Cohesive within composite	0	0	0	0	0	0
Mixed	1	1	0	4	0	0

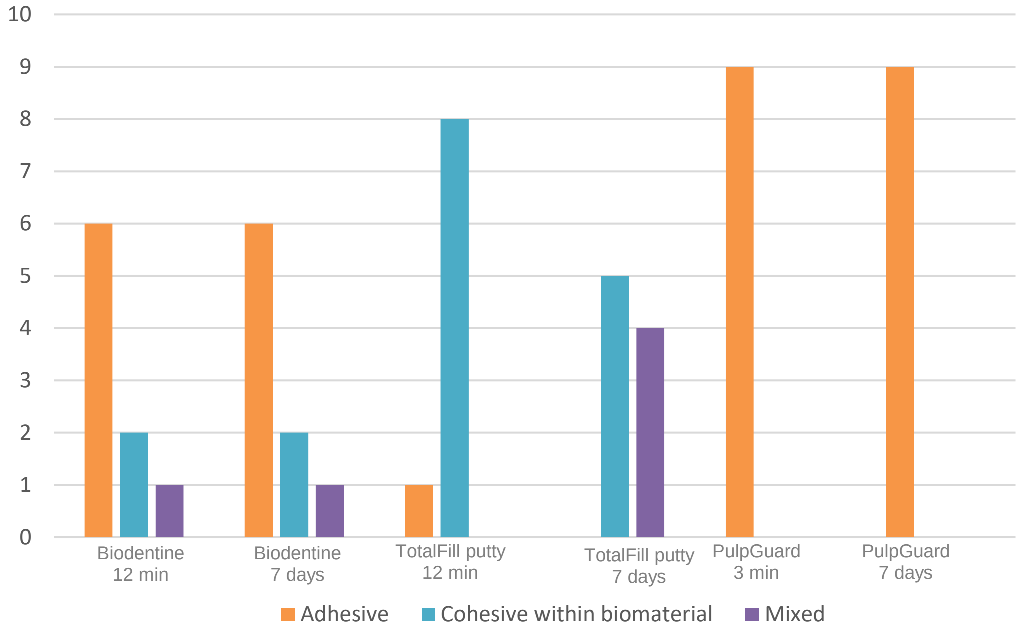

Figure 3 – Graphic showing fracture modes of the tested groups after shear bond strength tests.

There were no cohesive (Table 5 and Figure 3) failures within the restorative material (SDR).

Biodentine fractures were mostly adhesive, equally for 12-minutes group and 7-days group. Cohesive fractures within the biomaterial and mixed failures in both immediate and delayed groups also occurred.

TotalFill putty samples exhibited predominantly cohesive fractures within the biomaterial, with a higher rate for 12-minutes group. Mixed failures were observed for the delayed group and only one adhesive failure for the immediate group.

All PulpGuard samples presented adhesive fractures in both immediate and delayed material placement.

According to Ficher's exact test ($p<0,001$), there is a statistically significant association between the fracture type and the biomaterial. Biodentine and PulpGuard presented higher values of adhesive fractures. Opposite to these findings, TotalFill putty showed mostly cohesive fractures within the biomaterial.

The null hypothesis states that there are no statistical differences between the six tested groups concerning to shear bond strength values. Regarding the statistical meaningful differences ($\chi^2(5,47) = 5.966$; $p<0.001$), the null hypothesis has been rejected.

Discussion

After pulp capping materials placement, performed in VPT procedures, an effective bonding between the final restoration and the biomaterial is important to a successful treatment.[1,2] A wide diversity of protocol designs with different adhesive strategies and composite types do not allow a comparison between studies, rendering it difficult to develop guidelines. Therefore, to ensure success of conservative pulp treatments, the conception of a restorative protocol is crucial. Literature remains unclear concerning the proper timing to perform the definitive restoration, as well as which should be the suitable adhesive strategy.[1,7,12,25]

Odabaş *et. al* [27] evaluated the shear bond strength of etch-and-rinse and self-etch adhesive systems to Biodentine and found that the highest bond strength value was reached with self-etch adhesive systems, where the two-step self-etch adhesive (Clear Fill SE Bond) had the higher shear bond strength, compared with the one-step self-etch adhesive (Clear Fill S Bond). Meraji *et. al* [12] stated that the shear bond strength of three different dentin replacement materials (Biodentine™, Theracal LC and Fuji IX) was lower when a one-step self-etch adhesive was used, mainly for Biodentine samples. Hashem *et al.* [28] found no statistically significant differences between using a universal adhesive in etch-and-rinse or self-etch strategies when Biodentine was used as a pulp capping material. It has been suggested that etching Biodentine induces destruction of the microstructure and improves the leakage through the biomaterial/composite interface.[29] Anastasiadis *et al.* [30] refer that treating Biodentine's surface with phosphoric acid followed by the application of Heliobond is the best strategy. The authors also avowed that the chemical composition of Biodentine changed after the application of phosphoric acid, by the formation of a Ca-phosphate precipitate.[30] As referred, the application of phosphoric acid on Biodentine showed mechanical and chemical changes on the biomaterial surface.[12,28] The are few studies evaluating the etching effect on Biodentine's surface, and no evidence is available for PulpGuard and TotalFill® BC RRM™ putty. Concerning this fact, the bonding strategy used in the present study was a two-step self-etch adhesive technique, as these are described to be the most effective and long lasting alternative for dentin.[31] The most widely used monomer in adhesive systems is HEMA (2-hydroxy-ethyl-methacrylate).[32,33] Bakopoulou *et al*.[34] refers that free HEMA might disturb the odontogenic differentiation potential of pulp stem cells, promoting severe consequences for pulp tissue repair. According to these findings it would be clinically valuable to evaluate the penetration potential of adhesive systems with HEMA monomer into the biomaterials, as well the efficacy of HEMA-free adhesive systems in VPT procedures. Furthermore, it has been suggested that the functional monomer 10-methacryloyldecyl dihydrogen phosphate (10-MDP), present in the two-step self-etch adhesive system used in this study, may bind to the calcium in calcium silicate cements, as it happens to the one present in hydroxyapatites, promoting chemical bond in addition to micromechanical attachment.[28] The functional monomer can form hydrolytically stable 10-MPD salts, by the ionically interacting with calcium and making the adhesion interface more resistant to degradation.[31] Regarding the application of the two-step self-etch adhesive system, the active application of the bonding system was not performed at the immediate groups in order to prevent the disintegration of the recently placed biomaterials, thus consisting a limitation of the study.

There is no available evidence to propose a restorative protocol to perform after VPT procedures. However, considering the development of new calcium silicate cements, with distinct setting times, it is clinically relevant to determine the proper restorative timing for each biomaterial. The bioceramic materials used in this study exhibit different setting times. The biomaterial that presents a shorter setting time is PulpGuard, 3 minutes.[21] Biodentine's setting time is 12 minutes, while TotalFill putty has the longer setting time of approximately 2 hours.[7,12,18] There are few studies evaluating the shear bond strength of Biodentine to composite resins. Concerning PulpGuard and TotalFill putty, a limitation for comparison is the lack of scientific literature available. Hashem *et al.* affirmed that Biodentine must be overlaid with a composite resin two weeks after the placement of the biomaterial to allow intrinsic maturation that can withstand the contraction forces of composites.[28] In the other hand, Palma *et al.* [26] refers that there are no statistically significant differences between the immediate or delayed placement of the final restoration when using Biodentine, but the authors suggest that the desirable clinical approach is to perform the complete treatment in the same appointment. Obadas *et al*. [27] compared the shear bond strength at 2 different times, 12 minutes and 24 hours, and sustained that Biodentine showed better SBS values at 24 hours.

Concerning the immediate groups, Biodentine samples showed the highest mean shear bond strength value, with no statistically significant differences (p>0,05) compared with both TotalFill putty (group 3) and PulpGuard (group 5) groups. Regarding the 7-days groups, Biodentine (group 2) presented the highest mean shear bond strength value, with statistically significant differences (p<0,05) when compared with 7-days PulpGuard group (group 6).

Regarding intragroup analysis, no statistically significant differences were observed between both immediate and delayed groups. Our findings concerning to Biodentine are in agreement with the literature.[26] These results suggest that it is clinically valuable, for all three biomaterials to perform the final restoration at immediate timeframe, reducing costs as time.

One of the most critical factors to bear into consideration is the bond strength between the restorative material/dental surface and restorative material/biomaterial.[35] Thus, the shear bond strength values required to resist the contraction forces, producing gap-free margins, range between 17 and 20 MPa.[35,36] However in the present study the highest shear bond strength value was 15,88 MPa (Table 3) for the 7-days TotalFill putty group (group 4). Despite the lack of statistically significant differences (p>0,05) concerning immediate and delayed TotalFill putty groups, our findings report lower mean shear bond strength values for the 12-minutes group.

A recent study portrayed the importance of thermocyling the specimens to simulate the oral cavity conditions.[12] However the authors indicate that composite resins bonded with a self-etch adhesive system were totally lost after the thermocyling procedure.[12] According to these findings, the decision to thermocyle the samples may be important for future research.

In the present study, at one week of storage in an incubator, the biomaterial's surface presented an amorphous aspect with discoloration of the margins, potentially from the reaction of the metallic blocks components with the water, thus delayed samples were polished with an abrasive paper, aiming to regularize the biomaterial's surface and mimic clinical reality.

In our study no specimens presented cohesive fractures within composite resin, likewise Palma *et. al* [26] and Odabaş *et al* [27] findings. It has been suggested that bonding is acceptable when the fractures are cohesive within the biomaterial, contrary to the occurrence of adhesive fractures.[37] A cohesive failure within the pulp capping material represents the strength of the biomaterial itself and does not necessarily reflect the interfacial bond strength of composite/biomaterial.[28] Our findings suggest that Biodentine samples presented a higher rate of adhesive failures for both immediate and delayed groups. Conversely, Meraji *et al*. results showed a prevalence of cohesive failure within the biomaterial, reflecting the low strength of the Biodentine itself.[12]. TotalFill putty specimens presented mostly cohesive fractures within biomaterial, especially for the 12-minutes group. All PulpGuard samples showed adhesive fractures that could be explained by the biomaterial silicone composition, conveying a smoother and less porous surface, which might hinder the penetration of the adhesive system, compromising bonding. Additionally, during the bonding procedures, when applying the primer of the two-step self-etch adhesive, the biomaterial showed an hydrophobic behavior, preventing the primer from remaining on its surface. These findings could be an explanation for the lowest shear bond strength values observed in PulpGuard samples.

Conclusions

Within the limitations of this in vitro study, Biodentine and TotalFill putty have shown superior shear bond strength results when compared with PulpGuard, within delayed restorations (7-days). Our findings suggest that Biodentine allows restorative procedures immediately after pulp-capping biomaterial placement (12 minutes), requiring one single appointment to complete the procedure.

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