Longevity of Bond Strength of an Indirect Composite Resin to Dentin Using Conventional or Self-Adhesive Resin Cementation: Influence of Dentin Pretreatment with TiF_4

Keywords

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ABSTRACT

The purpose was to evaluate the influence of dentin pretreatment with titanium tetrafluoride (TiF_4) on the longevity of bond strength (BS) of an indirect composite to dentin, using conventional resin cementation strategy or a self-adhesive resin cement. Forty third human molars with exposed dentin surfaces were used. The teeth were divided into groups (n = 10), according to the cementation strategy and the presence or absence of pretreatment with TiF_4. Microtensile strength testing and failure mode analysis were performed after 24 hours, 180 and 360 days of storage in water. Split-plot ANOVA and Tukey's test showed that BS was significantly higher when the conventional strategy was used, regardless of the time period, and of the application or no application of pretreatment with TiF_4 ($p < 0.0001$). When TiF_4 was used for both cementing strategies, BS was lower after 360 days ($p = 0.0019$). Both cementing strategies led to the formation of a shallow hybrid layer, regardless of the presence of TiF_4. BS was higher when the conventional cementation strategy was used, regardless of TiF_4 pretreatment. TiF_4 used as a pretreatment agent associated with different types of resin cementation was unable to maintain adhesive bond strength in the long term.

INTRODUCTION

Conventional resin cements require the application of adhesive systems, which bond to the dental structure by forming a hybrid layer.[1] However, not all dual-cure conventional resin cements may combine with all self-etching adhesive systems - which may facilitate cementation procedures - due to the presence of amines in their composition, and some dentists may not follow the recommendations given by the manufacturers. On the other hand, self-adhesive resin cements were developed for the purpose of simplifying the cementation technique in a single step, since they do not require any adhesive pretreatment of the dental substrate. They are also characterized by multifunctional acid monomers that promote adhesion by micromechanical retention, leading to the formation of a hybrid layer. The hybrid layer seem to be superficial and very irregular, unable to demineralize the smear layer.[2] The likely result is the formation of an irregular layer between the cement and the substrate,[3] of no more than one micrometer on the surface of the dentin.[1,2]

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The degradation of the hybrid layer occurs over time and is due to several factors. Hydrolysis of the resin components and the organic matrix in the hybrid layer results from susceptibility of the adhesives to the sorption of water and oral fluids. Exposure of collagen fibers occurs, in general, not only when conventional adhesive systems but also self-etching universal adhesive systems are used.[4,5,6] In addition, degradation of exposed collagen fibers in the decalcified dentin is triggered by enzymes hosted by human saliva, known as matrix metalloproteinases (MMPs). All these factors impair the bond interface and result in loss of adhesive bond strength in the long term.[7,8]

Titanium tetrafluoride (TiF_4) have been evaluated as a dentin pretreatment strategy to inhibit demineralization at the enamel and dentin/restoration interface, because incorporation of the TiF_4 into the hybrid layer may result in a biomodified hybrid layer agent.[9,10] Its mechanism of action promotes the formation of a glaze-like vitreous layer on dentine, composed of titanium oxide or organometallic complexes.[11] This titanium compound, in contact with the organic material present in dentin, can form a stable coating, resistant to acids and alkaline solutions.[12,13] Thus, the application of TiF_4 on dentin would lower the risk of secondary caries lesions, and promote greater bond longevity, by modifying the smear layer, and ultimately benefiting restorative procedures.[10,14]

The use of 2.5% TiF_4 did not influence the bond strength with 115 or 2-step,[15,16,17] self-etching adhesive systems, but increased the bond strength to dentin when using a conventional 2-step adhesive system.[14] It has also been reported that TiF_4 does not influence bond strength to dentin over time, especially when incorporated into the adhesive or the primer.[17,18] However, the application of TiF_4 as a pretreatment associated with conventional or self-adhesive cementing agents has not been studied, suggesting that this treatment would provide a modified layer to increase the inhibition of secondary lesions formation,[19,20,21] without compromising bond strength to dentin.

Therefore, the purpose of this study was to evaluate the influence of TiF_4 on the bond strength of ceramic to dentin, using conventional and self-adhesive resin cementing agents. The null hypotheses to be tested was that TiF_4 does not influence the longevity of the bond strength of a ceramic to dentin, regardless the type of the cementing agent.

MATERIALS AND METHODS

After approval by the Research Ethics Committee (#51331615.6.0000.5374), forty sound and newly extracted human third molars were cleaned with a periodontal curette and maintained in a 0.1% aqueous thymol solution for use in this study. Flat surfaces of human dentin were obtained from the crown of human third molars. The roots of the teeth were removed 2 mm below the cementoenamel junction with a diamond disk mounted on a precision electric cutter (Isomet 1000 Precision Diamond Saw, Buehler Ltd, Lake Bluff, IL, USA). Afterwards, the occlusal enamel portion was removed, obtaining a flat, exposed superficial dentin surface on the occlusal third, perpendicular to the long dental axis. The fragments were transferred to a water-cooled rotary polisher (Politriz Aropol 2V, Arotec, Cotia, SP, Brazil) using aluminum oxide abrasives sandpaper (Imperial Wetordry, 3M, Sumaré, SP, Brazil), in descending order of granulation, (400, 600 and 1000) to obtain smooth dentin surfaces.

The pulp chamber exposed after removal of the roots was filled with dental composite (Filtek Z350 XT, 3M ESPE, Saint Paul, MN, USA) after application of the universal self-etching adhesive system (Scotchbond Universal, 3M ESPE, Saint Paul, MN, USA). Then, the teeth were separated into the groups designated for application or non-application of dentin pretreatment and the resin cements of these adhesive systems (n = 10), according to Table 1.

Table 1. Groups under study and number of teeth according to the realization or not of pretreatment in dentin and resin cements

Groups/ Acronyms	Number of teeth	Treatment
RelyX U200/ RU	10	Absence of pretreatment and application of self-adhesive resin cement
RelyX ARC/ RARC	10	Absence of pretreatment and application of conventional dual resin cement
Titanium tetrafluoride + RelyX U200/ TRU	10	Pretreatment with titanium tetrafluoride and application of self-adhesive resin cement
Titanium tetrafluoride + RelyX ARC/ TRARC	10	Pretreatment with titanium tetrafluoride and application of conventional dual resin cement

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The TiF_4 to be used for dentin pretreatment was obtained in pro-analysis form (PA) (Sigma Aldrich, Saint Louis, MO, USA), manipulated at a concentration of 2.5% in distilled water and deionized (weight: volume and pH = 1.4), as suggested by Dündar *et al.*[9] and used by Bridi *et al.*[15] and Domingues *et al.*[16] The product was applied to the dentin surfaces in the respective groups for 60 seconds, with active application, using a disposable brush followed by brief air-drying for 5 seconds, without previously removing the smear layer, as indicated by the manufacturers' indications for the adhesive system and resin cement used. The adhesive cementation protocols were then applied to the respective groups, according to the cementing agents and the manufacturers' guidelines *(Table 2)*.

After application of the resin cements, a ceromer block (Sinfony, 3M ESPE, Saint Paul, MN, USA) [monomer 48%, initiator system 1%, glass (silica) 40%, SiO_2 (silicon dioxide) 5%, GIC (special glass ionomer) 5%, silane 1%], 5.0 mm wide x 5.0 mm deep x 6.0 mm high, was cemented onto the dental element and photoactivated for 40 seconds. The ceromer blocks were pretreated with 50 µm aluminum oxide particles (Cojet, 3M / ESPE) for 15 to 20 seconds and silanized (Shannon, 1998). A 3-kg weight was used to press the block into position during cementation.

A LED light photoactivator was used (VALO LED curing light, Ultradent, Salt Lake City, UT, USA) to photoactivate the adhesive system and the conventional and self-adhesive resin cements. The high intensity polymerization mode was used: 1000 mW/ cm^2 for 40 seconds, 10 seconds on each face.

The dentin blocks receiving ceromer cementation were fixed in acrylic plates for positioning in a metallographic cutter (Isomet 1000 Precision Diamond Saw, Buehler Ltd, Lake Bluff, IL, USA). Vestibular-lingual and mesial-distal cuts were performed, obtaining specimens with cross sections of approximately 1 mm^2. The sticks were stored in Eppendorf tubes, in distilled water, in an incubator, at 37°C. After 24 hours, one third of the sticks were subjected to microtensile bond strength testing. After 180 days, half of the remaining sticks were submitted to the microtensile bond strength test, whereas the other half were submitted to the same test after a storage period of 360 days. The water used for beams storage was renewed weekly.

Microtensile bond strength tests were performed in a test machine (EZ Test, LX 5kN, Shimadzu, Kyoto, Japan) at a speed of 0.5 mm/ min and a 50N load cell. The sticks were glued at the ends and tested in a specific device for performing microtensile bond strength tests (Superbonder, Henkel Loctite Ltda, São Paulo, SP, Brazil). The bond strength values were obtained in MPa.

The surfaces of the fractured specimens were examined visually by a stereoscopic magnifying glass with 40X magnification to classify the fracture type. The following fracture types were observed: adhesive (adhesion failure), cohesive in enamel or dentin (dental substrate failure), cohesive in resin (composite resin failure) or mixed (adhesive and cohesive failure in resin).

Table 2. Cementing agents used, composition, use protocol and manufacturer

Cementation agents (lot number)	Composition	Use protocol	Manufacturer (city, state, country)
RelyX U200 (604334)	Base paste: silane treated glass powder, 2-propenoic acid, 2-methyl 1,1 '- [1- (hydroxymethyl) -1,2-ethanediyl], ester, triethylene glycol dimethacrylate (TEG-DMA), silica treated with silane, glass fiber, sodium persulfate and t-butyl per 3,5,5-trimethylhexanoate. Catalyst paste: silane treated glass powder, substituted dimethacrylate, silane treated silica, sodium p-toluenesulfonate, 1-benzyl-5-phenyl-baric acid, calcium salts, 1,12-dodecane dimethacrylate, calcium hydroxide and titanium dioxide	Dispense self-adhesive resin cement, mix and apply over dentin.	3M ESPE (Saint Paul, MN, USA)
RelyX ARC (1705800537) + Scotchbond Universal (589525)	Rely X ARC Paste A: Bis-GMA, TEGDMA, silica zirconia, pigment, amine, photoinitiator system. Paste B: Bis-GMA, TEGDMA, silica zirconia, benzoyl peroxide Scotchbond Universal Bis-GMA, HEMA, dimethacrylates, polyalkenoic acid, copolymer, water, ethanol	Apply the universal self-etching adhesive actively with a disposable brush for 20 seconds and photoactivate for 10 seconds. Dispense conventional resin cement, mix and apply over dentin.	3M ESPE (Saint Paul, MN, USA)

Bis-GMA: bisphenol-glycidyl methacrylate; HEMA: 2-hydroxyl methacrylate; MDP: 10-methacryloyloxydecyl dihydrogen phosphate; TEGDMA

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Before obtaining the sticks for the tests, one or two slices from each tooth were separated to perform scanning electron microscopy of the tooth-restoration interface at 24 hours evaluation. The specimens were mounted on aluminum stubs and received gold coverage for 60 seconds. Then they were examined under a scanning electron microscope (Jeol 5900LV, Jeol Ltd, Tokyo, Japan) at a voltage of 10 Kv. Each specimen had the full extent of the adhesive interface carefully traversed at 500X magnification. The most representative area of each specimen was photographed at the same magnification, and at magnification of 1000X. The morphology of the interface was analyzed in relation to the hybrid layer formation, analyzing its integrity and thickness, as well as the presence, size and arrangement of the tags.

After the exploratory analysis (graphic evaluation of the studentized residuals to verify the presence of outliers and the homogeneity of variance; and the error normality by the box plot, quantile-quantile (Q-Q) blot and Shapiro-Wilk test), the microtensile bond strength data in MPa were submitted to analysis of variance (ANOVA) in split plot designs, where the plots were represented by the cement types and pretreatment, and the subplots, by the storage time. Multiple comparisons were performed using the Tukey test. In this analysis, the teeth were considered as experimental units, and those with early failure were discarded. A frequency distribution table was devised according to the number of sticks with early failure per treatment and time. The comparison of the stick fracture pattern among the groups was performed using the Fisher Exact test. The analyses were performed in SAS (SAS Institute Inc., Cary, NC, USA, Release 9.2, 2010) and R software (R Core Team, Vienna, Austria, 2015), considering a significance level of 5%.

RESULTS

There was no triple interaction among the factors under study: pretreatment * cement * time * (p = 0.4263). The mean bond strength was significantly higher for the conventional cement strategy at all the time periods, regardless of application or no application of 2.5% TiF_4 pretreatment (p <0.0001). In the group without pretreatment, there was no significant difference between the two resin cements in relation to the time periods (p> 0.7591). In the pretreatment group, the mean bond strength was significantly lower at 360 days than at 24 hours (p = 0.0437) for the two cements, but especially in the case of the conventional cement (Rely X ARC), when 2.5% TiF_4 pretreatment was applied (p = 0.0121) *(Table 3)*.

In the 24-hour period, the percentage of pre-failure sticks ranged from 0% for the conventional cement without TiF_4 pretreatment to 20% for the self-adhesive cement with pretreatment. In the 180-day period, the percentage of failures ranged from 0% for the conventional cement to 7.7% for the self-adhesive cement. At 360 days, the percentage difference between the self-adhesive cement with versus without pretreatment ranged from 12.1% to 13.3%, respectively *(Table 4)*.

There was an association between the groups and the fracture pattern at all the time periods (p <0.05) *(Table 5)*. At 24 hours, adhesive fracture was observed for most of the sticks in the self-adhesive cement group both with and without pretreatment, and also in the conventional group with pretreatment. As for the conventional cement group without pretreatment, 55% of the sticks had cohesive fracture in resin. Only the conventional cement presented fracture in resin. At 180 days, most of the sticks had adhesive fracture in all the groups, but the conventional cement also had other fracture types. At 360 days, the conventional cement both with and without pretreatment, as well as the self-adhesive cement with pretreatment, presented cohesive fracture in resin. It is noteworthy that most of the sticks in all the groups presented adhesive fracture at 360 days.

Table 3. Mean (standard deviation) bond strength (MPa) based on cement pretreatment with titanium 2.5% tetrafluoride and storage time

Pretreatment	Cement	Storage time		
		24 hours	180 days	360 days
Absent	Self-adhesive	14.56 (7.12) Ab	9.19 (4.15) Ab	13.47 (9.10) Ab
	Conventional	*42.13 (15.52) Aa	*35.24 (11.26) Aa	*40.59 (13.28) Aa
Present	Self-adhesive	14.39 (7.60) Ab	8.14 (3.40) ABb	8.00 (6.23) Bb
	Conventional	31.27 (16.38) Aa	28.02 (11.25) ABa	21.15 (10.73) Ba

Mean followed by distinct letters (uppercase horizontally and lowercase vertically compare the two cements with each pretreatment) indicates a significant difference (p≤0.05). * indicates values that differs from those of the pretreatment group, under the same conditions of cement and time (p≤0.05)

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Table 4. Frequency (%) of early failures based on cement, pretreatment with 2.5% titanium tetrafluoride and storage time

Pretreatment	Cement	Storage time		
		24 hours	180 days	360 days
Absent	Self-adhesive	5 (12.5%)	2 (7.7%)	4 (13.3%)
	Conventional	0 (0.0%)	0 (0.0%)	4 (12.9%)
Present	Self-adhesive	8 (20.0%)	2 (7.7%)	4 (12.1%)
	Conventional	3 (7.5%)	0 (0.0%)	5 (13.2%)

Table 5. Frequency distribution of the fracture pattern based on cement, pretreatment with 2.5% titanium tetrafluoride and storage time

Time	Pretreatment	Cement	Fracture Pattern			
			Adhesive	Mixed	Cohesive in dentin	Cohesive in resin
			n (%)	n (%)	n (%)	n (%)
24 hours	Absent	Self-adhesive	34 (94.4%)	2 (5.6%)	0 (0.0%)	0 (0.0%)
		Conventional	16 (40.0%)	1 (2.5%)	1 (2.5%)	22 (55.0%)
	Present	Self-adhesive	32 (100.0%)	0 (0.0%)	0 (0.0%)	0 (0.0%)
		Conventional	25 (67.6%)	6 (16.2%)	2 (5.4%)	4 (10.8%)
			p-score < 0.0001			
180 days	Absent	Self-etching	23 (95.8%)	1 (4.2%)	0 (0.0%)	0 (0.0%)
		Conventional	19 (52.8%)	2 (5.6%)	4 (11.1%)	11 (30.6%)
	Present	Self-etching	24 (100.0%)	0 (0.0%)	0 (0.0%)	0 (0.0%)
		Conventional	25 (75.8%)	2 (6.1%)	1 (3.0%)	5 (15.2%)
			p-score = 0.0002			
360 days	Absent	Self-etching	26 (100.0%)	0 (0.0%)	0 (0.0%)	0 (0.0%)
		Conventional	19 (70.4%)	0 (0.0%)	0 (0.0%)	8 (29.6%)
	Present	Self-etching	29 (96.7%)	0 (0.0%)	0 (0.0%)	1 (3.3%)
		Conventional	31 (93.9%)	0 (0.0%)	0 (0.0%)	2 (6.1%)
			p-score = 0.0010			

The micromorphological evaluation (*Figure 1*) showed that there were few resin tags at the adhesive-cement interface, for both the self-adhesive (*Figures 1A and 1C*) and the conventional cement (*Figures 1B and 1D*). Application of the conventional cement led to the formation of a shallow hybrid layer, regardless of the presence or absence of pretreatment.

DISCUSSION

The present study showed that the microtensile bond strength was significantly higher when using conventional rather than self-adhesive cement, at all the time periods, corroborating the findings in the literature.[22,23] The cement-dentin interface is morphologically different in relation to both the conventional and

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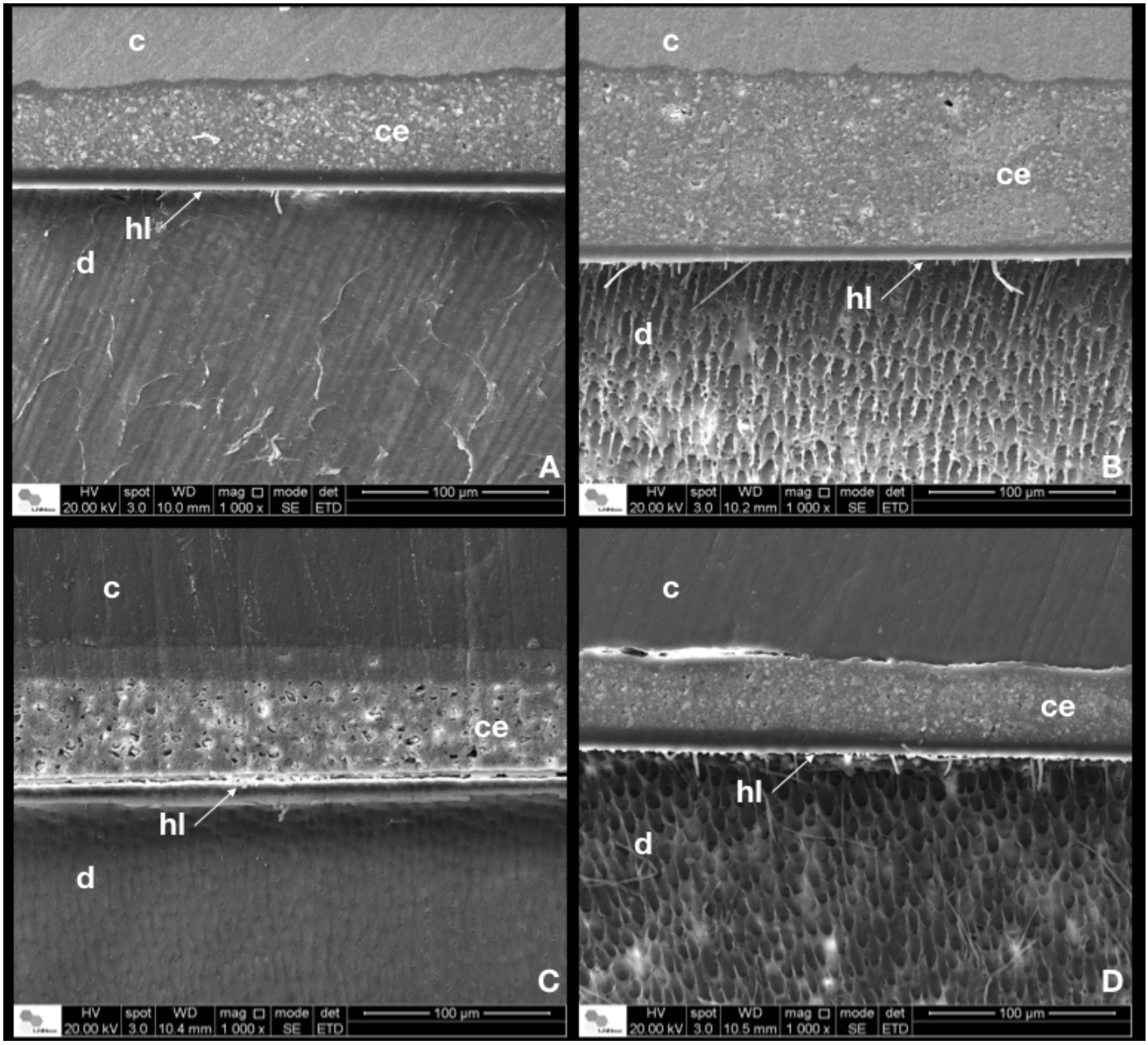

Figure 1: Adhesive interface micromorphology (24 hours evaluation). A) Application of self-adhesive cement; B) Application of conventional cement; C) Dentin pretreatment with TiF_4 and applying the self-adhesive cement; D) Dentin pretreatment and application of conventional cement; c) Ceromer; ce) Cement; hl) Hybrid layer; d) Dentin.

the self-adhesive cements. The formation of a classic hybrid layer does not occur with self-adhesive cements, which promote minimal interaction with the dentin substrate.[2,3] Not only is this interaction superficial and irregular, but the hybrid layer is not very thick, and there is minor or no resin tag formation. This was corroborated micromorphologically in the present study, which found the formation of a few resinous tags at the adhesive interface, when self-adhesive cement was used.[2]

In this respect, the bond obtained is dependent not only on micromechanical retention, but mainly on the chemical interaction between the acid monomer groups and the hydroxyapatite of the dental substrate. The acidic hydrophilic monomers simultaneously demineralize and infiltrate the dental substrate, becoming hydrophobic after polymerization and providing micromechanical retention. In addition, the phosphate groups of the functional monomers include a mixture of monomers which react with the hydroxyapatite of the dental substrate, resulting in additional retention by chemical bonding.[24] However, the acidic monomers have low etching capacity, minimizing surface demineralization,[24] besides the buffering effect of the minerals in the dentin that neutralizes the cement pH.[25] Another concern regards to the high viscosity of the cement that hinders its penetration into the interfibrillar space associated to the non-removal or incomplete removal of the smear layer, which promotes a weak bond with the resin's intermediate layer.[24] The multifunctional phosphoric acid methacrylate monomers in the self-adhesive cements is capable of etching dental hard tissues and interacting with the tooth substance. An ionization process occurs in situ, using water associated with the dentin or produced during neutralization of the phosphate monomers by basic filler materials.[26]

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Bonding occurs between the Ca ions associated with the hydroxyapatite component of dentin and the ionized phosphoric acid groups of the monomer mixture, creating $Ca_3(P_5{+}O_4)_2$ in phosphate-based cements and $CaHO_3P_3{+}$ in phosphonate-based cements.[26]

Conventional resin cements require the application of adhesive systems to bond to the dental structure by hybrid layer formation. The process of micromechanical bonding depends on the strategy and the type of adhesive used. Whereas conventional adhesive systems promote total removal of the smear layer and demineralization of the dentin surface by application of phosphoric acid, self-etching adhesive systems partially remove the smear layer. In this case, there is no subsequent removal of the dissolved calcium phosphates, since they are not rinsed out.[1,27] In addition, the self-etching adhesive system used in this study contains MDP, which establishes a chemical bond with the hydroxyapatite and provides better stability than the micromechanical retention obtained with conventional adhesive systems.[28] Although the manufacturer of the self-etching adhesive system evaluated in this study recommends the use of a amine-free resin cement (as RelyX Ultimate), some dentists may not follow the recommendation and combines different resin cements and adhesive systems. However, the bond strength values achieved were higher than those achieved by the self-adhesive resin cements, regardless the occurrence of the peroxide-amine redox system and the pH value of the adhesive system used.

The micromorphological analysis showed that the application of the conventional cement associated to the self-etching universal adhesive system led to the formation of a slightly greater number of resinous tags in the hybrid layer, compared to use of self-adhesive resin cement alone, although a shallow hybrid layer was also obtained due to the use of a universal adhesive system in a self-etch mode. Each adhesive system shows particular hybridization quality and bond strength, which depends upon not only the strategy of the adhesives, but also on the composition of the adhesives and the interaction to dentin.[28] Scotchbond Universal may be classified as a mild self-etch adhesive when it is used in the self-etch mode, creating hybrid layers that are approximately 0.5 mm thick.[28] Although the presence of longer tags and higher thickness of the hybrid layer are not related to higher bond strength values,[28] it was observed that the cohesive in resin failure type was more prevalent in the conventional cementation strategy at 24 hours. This can be attributed to the presence of the functional monomer 10-MDP and the hydroxyethyl methacrylate (HEMA) which provides chemical interaction with the apatite crystallites, to the thin hybrid layer obtained,[28] and also to the presence of amine of the resin cement used (which is not what manufacturers recommend), which could contribute to a higher prevalence of cohesive than adhesive failures.

Most dual-cure resin cements, including RelyX ARC, are based on a peroxide-amine redox system. The pH of Scotchbond Universal is around 2.7, which is in the borderline of being compatible with resin cements with a peroxide-amine redox system (manufacturers' information). The adhesive system used must be mixed with a dual cure activator, as recommend by the manufacturer, or must be used with an amine-free resin cement (RelyX Ultimate). Simplified adhesives can lead to the deactivation of the amine initiators in dual-cure composites, since the incorporation of acidified resin monomers into the primer-adhesive combination, results in a more hydrophilic mix. The concentration of acidic resin monomers is even higher in universal adhesive systems,[28] which can deactivate tertiary amines, as it occurs for the self-etching adhesive systems,[29] which may have contributed to higher cohesive failures.

Some studies have shown that self-adhesive resin cements exhibit similar bond strength to dentin or yield results even superior to conventional resin cements, when pretreatments (such as polyacrylic acid and phosphoric acid) are used, because they remove or modify the smear layer.[1,2,30,31] However, studies on self-adhesive resin cements that use a pretreatment and that yield superior bond strength would ultimately question the use of these cements, considering that their main advantage is to make the application technique easier by reducing the clinical cementation steps. Only the study by Turkmen *et al.*[31] showed that the bond strength of self-adhesive cements was superior to conventional cements. In their study, the results were attributed to the multifunctional methacrylates of phosphoric acid in the organic matrix of these cements.

When no TiF_4 pretreatment was used, the bond strength and the failure types found for both cements evaluated in our study were similar among the time periods. Some authors report that the water formed in the process of neutralizing the self-adhesive resin cements promotes their initial hydrophilicity. This leads to better adaptation of the cement to the dental structure. Subsequently, this water is reused to trigger the reaction with the functional acid groups, as well as the reaction of the cement with the ions liberated from the alkaline-charged particles.[1,32] Hence, this reaction results in a hydrophobic matrix with low solubility and greater stability over time.[1,32] It is likely that the bond strength values were not significantly different because of the short evaluation time, which was 12 months for both cements. Evaluation after longer storage periods could lead to greater degradation of the cement and/or adhesive by water, since hydrolytic degradation of the hybrid layer may result in disintegration of collagen fibrils devoid of mineral or resin cover.[2] In addition, the presence of water in the extracellular matrix is also directly related to metalloproteinases (MMPs) activity.

It is known that hydrolytic degradation of resin in the interfibrillar spaces of the hybrid layer is capable of weakening the bond strength. Resin hydrolysis is a process capable of breaking the covalent bonds between the polymers, and ester bond hydrolysis causes loss of resin mass. Resin degradation is directly related to the water sorption of the resins, adhesives

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and the organic matrix network.[33] The present study used a self-adhesive and a conventional resin cement combined with a self-etching adhesive system. Neither strategy cementation technique exposes the collagen fibrils, because there is no removal of the smear layer when treated with phosphoric acid. However, hydrolytic degradation may occur if a longer storage time than that used in the present study were contemplated, which should be further evaluated in future studies.

Dentin pretreatment with a TiF_4 aqueous solution ultimately aims at preserving bond longevity and reducing the incidence of secondary caries lesions, by promoting the formation of a stable coating resistant to acids, and providing greater resistance of the substrate when dental demineralization occurs,[10,13-20] because of smear layer modification.[13,34] This modification consists of the formation of a vitreous layer of titanium dioxide on the surface, resulting from the bond between the titanium and the oxygen of the phosphate group.[11,13]

When using TiF_4 pretreatment associated to self-adhesive resin cement, the values for bond strength were similar to using self-adhesive cement with no pretreatment. However, after 360 days of storage, the mean bond strength when using TiF_4 pretreatment was lower, compared with 24 hours of storage time. The decrease in bond strength may have occurred in the groups where TiF_4 was applied, because its low pH of 1 to 1.3[21,35] has an acidic effect that can activate the metalloproteinases (MMPs) in dentin, leading to degradation of the hybrid layer. It is known that MMPs are activated when there is a reduction of pH in the dentin matrix.[36,37] After neutralizing the pH, previously activated MMPs degrade the collagen matrix,[37] leaving the partially demineralized dentin layer exposed and again susceptible to the action of acids. In addition, the use of TiF_4 pretreatment may have influenced adhesive bonding, since the dispersion of TiF_4 particles in water may have formed agglomerates that hinder penetration of the adhesive.[18] Therefore, future studies may consider the incorporation of TiF_4 into the resin cement composition as a strategy for removing additional pre-treatment steps and counteracting the effects of particles agglomeration in aqueous solution.

However, in regard to the conventional resin cement, the mean bond strength values were significantly lower at all the time periods when TiF_4 pretreatment was used. This could be attributed to the vitreous layer formed by the pretreatment application,[11,13] which may have reduced the amount of calcium available for the chemical bonding between the universal adhesive system and the dentin. As mentioned before, bonding between 10-MDP and dentin occurs mediated by the Ca ions,[28] which may have be compromised due to the TiF_4 pretreatment. This application may have also influenced the micromechanical bond by modifying the surface dentin, where hybrid layer formation occurs. Moreover, the micromorphological evaluation showed that the application of TiF_4 reduced the amount and length of the hybrid layer resin tags.

Although a decrease in the bond strength was not verified after 6 or 12 months, when using TiF_4 pretreatment associated to the two-step self-etching adhesive system,[17,18] chemical interactions may have occurred between the pretreatment and the adhesive cementation. This is because the lower pH of the acidic primer of a simplified adhesive system (when primer and bond are combined in a single step) and its hydrophilic nature make it incompatible with a dual-cure resin cement.[38] During the cementing process with chemical or dual resin cements using the simplified adhesive systems, oxygen inhibition causes the acid monomers of the non-polymerized adhesive layer to compete with the peroxides for the aromatic tertiary amine of the resin cement, resulting in an acid-base reaction at the adhesive-cement interface. In our study, this reaction may have been influenced by the presence of TiF_4.

The null hypotheses of this study was rejected, since TiF_4 influenced the longevity of the bond strength of a ceramic to dentin, regardless the type of the cementing agent. Bond strength decreased significantly over time when TiF_4 pretreatment was used with both cements types; furthermore, there was a significant reduction between the 24-hour and the 12-month time periods. This result may be related to the inherent degradation of the resinous materials exposed to the oral medium by water sorption. Consider that water promotes hybrid layer degradation, capable of plasticizing the polymers, and thus reducing the bond strength values. On the other hand, the decrease in adhesive bond strength promoted by the pretreatment could be related to the acid pH of the pretreatment solution. This acidity can cause enzymatic degradation of the hybrid layer collagen fibrils, because of its action on the metalloproteinases.[36,37] Moreover, TiF_4 agglomerates could have formed from its use as an aqueous solution.[18]

Although this study presents some limitations regarding the need for a longer time evaluation (longer than 12 months) for bond strength tests and the use of an aqueous solution of TiF_4 (which presents tendency for particles agglomeration), the results of the present study highlight the importance of the cementation strategy used to perform the resin cementation procedures. Although self-adhesive resin cements appear to be promising materials, because of their practicality and clinical acceptance, further studies on these materials are needed, especially regarding their long-term clinical performance. The basic issue regards their lower bond strength values in comparison with conventional cements combined with self-etching adhesive systems.

CONCLUSION

The use of TiF_4 pre-treatment with either cementation strategy does not seem to be indicated, since use of TiF_4 did not show superior results over time. The use of TiF_4 pre-treatment was shown to reduce the dentine bond strength of conventional resin cement (short and long term) and self-adhesive resin cement (long term). Therefore, further studies are needed in this regard, before clinical applicability of this procedure can be considered.

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