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Bond Strength and Interfacial Micromorphology of Etch-and-Rinse and Self-Adhesive Resin Cements to Dentin

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Keywords
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Abstract

Purpose: To evaluate the microtensile bond strength and interfacial micromorphology of indirect composite restorations to dentin using three commercial resin cements after 24 hours and 30 days of water storage.
Materials and Methods: The medium dentin of third human molars was exposed (N = 30, n = 10 per group). Three commercial resin cements were used to cement indirect resin composite restorations to dentin: the auto-cured C&B Cement/All Bond 2, the dual-cured RelyX ARC/Adper Single Bond 2, and the self-adhesive dual-cured RelyX Unicem. Teeth were sectioned after water storage at 37°C (24 hours and 30 days) to obtain beams with a bonded area of 0.8 mm^2. The specimens were tested in a universal testing machine at a 0.5 mm/min crosshead speed. Scanning electron microscopic fractographic and interfacial micromorphology analyses were performed. Data were analyzed using two-way ANOVA and Tukey's test ($\alpha = 0.05$).
Results: Mean bond strength (MPa) after 24 hours: C&B Cement 19.5 ± 3.8, RelyX ARC 40.8 ± 9.4, RelyX Unicem 31.3 ± 7.4; after 30 days: C&B Cement 24.5 ± 5.1, RelyX ARC 44.2 ± 8.5, RelyX Unicem 28.3 ± 7.1. The mean bond strengths of both dual-cure cements were significantly higher than that obtained with C&B Cement after 24 hours. A significant increase in the bond strength of C&B Cement was verified after 30 days, reaching values statistically equivalent to those produced by RelyX Unicem and RelyX ARC. The self-adhesive cement preserved the same level of bond strength after 30 days. Fractographic analysis revealed a prevalence of cohesive fractures in the hybrid layer for C&B Cement, mixed (cohesive in the cement, hybrid layer, and adhesive) for RelyX ARC, and cohesive in the cement for RelyX Unicem. No distinguishable hybrid layer or resin tags were observed in the interaction of RelyX Unicem with dentin.
Conclusions: The particular interaction of each cement with dentin results in specific bond strength and failure patterns that varied among groups in both evaluation times. Even though the self-adhesive cement tested exhibited no authentic hybrid layer, it was able to promote reliable adhesion with the underlying dentin.

The effectiveness of resin cements used for bonding indirect restorations is critical. A variety of factors can influence the performance of luting material, including the clinical scenario,[1] the polymerization method and degree of conversion,[2] the physical/chemical properties,[3,4] and the biologic aspect regarding the pulp response.[5] It has also been claimed that the adhesive system used in association with the cementing agents are of paramount importance in preventing an early dislodgement and providing long-term bonding stability.[2]

Resin cements are classified according to their activation reaction as self-cured (chemically activated), light-cured (photoactivated), or dual-cured cements (the combination of both activation reactions).[6] Based on the interaction with the tooth substrates, resin cements can be also classified into three categories: etch-and-rinse, self-etch, and a new group of resin cements known as self-adhesive systems.[7,8] The core idea behind the introduction of self-adhesive cements was to overcome to a certain extent the drawbacks seen when other types of cements are used to bond indirect restorations to the tooth tissues.[9] The cements of this group require no technique-sensitive steps such as acid-etching, priming, and bonding,[10] and they eliminate the possibility of chemical incompatibility that can occur when simplified adhesive systems are associated with self- or dual-cured resin cements.[11] Furthermore, there is no need for treatment of the internal surface of indirect composite restorations.[12] The pioneering commercial product in this group of cements was named RelyX Unicem (3M ESPE, St. Paul, MN). It has been claimed that this resin cement presents an acceptable film thickness[13] and causes less aggressive effects to the pulp-dentin complex in comparison to an etch-and-rinse resin cement.[5]

RelyX Unicem presents both a new methacrylate monomer formulation and technology of initiating polymerization in an acidic environment. These methacrylate monomers contain phosphoric acid esters that simultaneously demineralize and infiltrate both the smear layer and the underlying dentin, providing micromechanical bonding.[14] The polymerization process starts with the light exposure or through the self-curing mechanism. Cross-linked, high molecular-weight polymers are formed due to monomer conversion.[12] At the same time, a glass-ionomer concept was added to the formulation to neutralize the initial low pH, which increases from 1 to 6.[15] This cement reacts chemically with hydroxyapatite crystals in the dental tissues and with the vitreous particles of silicate aluminum fluoride present on its formulation. In a previous study,[14] the potential for chemical interaction between RelyX Unicem and hydroxyapatite was investigated, and a high chemical interaction with calcium derived from hydroxyapatite was confirmed. Thus, it was proven that this adhesion strategy relies not only on micromechanical retention, but also on chemical interactions between monomer acidic groups and hydroxyapatite.

The purpose of the present study was twofold: (1) to evaluate the bond strength of indirect composite restorations to dentin after 24 hours and 30 days of water storage; and (2) to characterize the interfacial micromorphology of the bonding region when different resin cements were used to bond indirect composite restorations to dentin. Resin cements were selected to represent a variety of commonly used classifications: a self-cured (chemically activated) cement (C&B Cement, Bisco, Inc., Schaumburg, IL), a conventional dual-cured resin cement (RelyX ARC, 3M ESPE), and a dual-cured, self-adhesive resin cement (RelyX Unicem). The dentin-bonding agents used in association with both dual-cured resin cements were manufactured by the same company. The following research hypothesis was tested when a chemically cured and two commercial dual-curing resin cements were compared: the bond strength values of the different groups would be similar, irrespective of evaluation time.

Materials and methods

Thirty-nine sound human third molars were selected for the present study. Teeth were obtained and used in accordance with a protocol approved by the Research Ethical Committee (Protocol #050/2006). Teeth were stored in chloramine T solution at 4°C and used within 4 months of extraction.[16]

Microtensile bond strength evaluation

Thirty human molars were then selected, and a flat dentin surface was exposed on each tooth after wet grinding the occlusal enamel with #180-grit SiC paper.[17] If the pulp was exposed, the specimen was discarded. The medium dentin surfaces were further polished with a wet #600-grit SiC paper for 60 seconds to standardize the smear layer.[18] Specimens were divided into three groups of ten teeth each, according to the technique used to cement an indirect composite restoration to the flat exposed dentin. Three commercial resin cements and their respective bonding agents were used. Table 1 contains the description of these materials.

Indirect composite resin disks were constructed with a second-generation, laboratory-processed resin (Symphony shade DA2, 3M ESPE) using a metallic mold (10 mm × 2 mm). The operative sequence to polymerize the indirect restorations followed the protocol established by the manufacturer. After restoration fabrication, the internal surfaces of the indirect restorations were sandblasted with 50 μm aluminum oxide glass spheres (Sandblaster Micro Etcher, Buffalo Dental, San Ramon, CA) for 10 seconds. Restorations were then ultrasonically cleaned in distilled water for 3 minutes. Silane primer (RelyX Ceramic Primer, 3M ESPE) was then applied with a mini-sponge to the internal surfaces of the indirect restoration when both 3M ESPE materials (RelyX ARC/Adper Single Bond 2 and RelyX Unicem) were used. Groups cemented with C&B Cement received silane Porcelain Primer (Bisco, Inc.). Both silane primers were applied in accordance with the manufacturer's instructions.

Cementation procedures are described in Table 2. Resin cements were dispensed onto a mixing pad and mixed. A thin layer of cement was applied to the internal surface of the indirect restorations and then slowly seated in position with gentle finger pressure. Thereafter, the teeth were placed in an apparatus with a constant seating pressure of 3.0 kg maintained for 3 minutes.[10] Excess cement was removed after setting, and each cement surface/margin was photoactivated using a conventional quartz-tungsten-halogen light (XL 3000 3M ESPE) operating at 500 mW/cm^2. C&B Cement needed no photoactivation. Specimens were then stored in a dark environment at 37°C and 100% relative humidity. After each storage time (24 hours and 30 days), the teeth were longitudinally sectioned in both "x" and "y" directions across the bonded interface using a diamond-impregnated disk (Extec, Enfield, CT) in a specific cutting machine (Isomet 1000, Buehler, Lake Bluff, IL), under water-cooling at 300 rpm. This resulted in bonded stick-shaped specimens with a cross-sectional area of 0.8 (± 0.2 mm^2). The stick area was measured with a digital caliper (Absolute Digimatic, Mitutoyo, Tokyo, Japan) after testing. Individual bonded sticks were positioned in a Universal Testing Machine (Instron model 4411, Canton, MA) by means of cyanoacrylate-based glue (Zapit, Dental Ventures of America, Corona, CA) and then subjected to tensile forces at a 0.5 mm/min crosshead speed of until failure. The results were recorded, and the ultimate tensile

Table 1 Materials used

Material	Manufacturer	Lot no.	Composition
Uni-Etch Acid	Bisco, Inc., Schaumburg, IL	0300014202	Phosphoric acid 32%, benzalconic chloride
All-Bond 2		0500008843	Primer A: NTG-GMA, acetone, ethanol, water
		0500008844	Primer B: BPDM, photo initiator, acetone
		0500008707	Pre-bond resin: Bis-GMA, TEGDMA, benzoyl peroxide, BHT
C&B Cement		0500011259	Base paste: Bis-GMA, Bis-EMA, silica
		0600001167	Catalyst paste: Bis-GMA, TEGDMA, silica
Scotchbond Etchant	3M ESPE, St. Paul, MN	4HP	Phosphoric acid gel 35%, sílica.
Adper Single Bond 2		4YE	Bis-GMA, GDMA, UDMA, HEMA, nanofiller, water, ethanol, methacrylate functional copolymer of polyacrylic and polyitaconic acids
RelyX ARC		FKGB	Bis-GMA, TEGDMA, dimetacrylate polymer, zircone, silica
RelyX Unicem		232722	Powder: glass powder, initiator, silica, substituted piramidine, calcium hydroxide, peroxide compound, pigments Liquid: methacrylate phosphoric ester, dimetacrylate, acetate, stabilizer, initiators.

Bis-GMA: Bis-phenol A diglycidylmethacrylate; BHT: butylated hydroxytoluene; NTG-GMA: N-tolylglycine glycidyl methacrylate; BPDM: biphenyldicarboxylic-acid dimethacrylate; Bis-EMA: Bisphenol A ethoxylated dimethacrylate; GDMA: glycerol dimethacrylate; HEMA: 2-hydroxyethyl methacrylate; TEGDMA: triethyleneglycol dimethacrylate; UDMA: urethane dimethacrylate.

Note: The brand name of Adper Single Bond 2 is used in Latin America and Oceania, while Adper Scotchbond 1 XT is used in Europe, Adper Single Bond Plus in the USA, and Adper Single Bond 1 XT in South Africa.

stress values were converted into MPa. Statistical analysis of each parameter was performed using two-way ANOVA among the different curing conditions (factors were resin cements and storage time). Tukey's HSD post hoc test was performed as a multiple comparison test at a preset alpha of 0.05.

Fractured specimens were stored in plastic containers (Eppendorf Multi-vials, Electron Microscopy Sciences, Fort Washington, PA) containing saline solution (0.9% sodium chloride) for 24 hours. Afterward, specimens were mounted on stubs with double-face carbon tape and desiccated in silica gel for 2 hours. Specimens were then sputtered (SCD 050; Balzers, Schaan, Liechtenstein) with a thin palladium-gold film (25 nm) for 100 seconds at 40 mA and examined by scanning electron microscope (SEM; JEOL-5600 LV, JEOL Ltd., Tokyo, Japan) operating at 15 or 20 kV. The failure modes were classified according to the following categories:[19] type I—cohesive fracture in the cement; type II—cohesive fracture in the hybrid layer; type III—mixed fracture (cohesive in the cement, hybrid layer and adhesive); type IV—mixed fracture (cohesive in the hybrid layer and adhesive); type V—mixed fracture (cohesive in cement and adhesive); type VI—mixed fracture (cohesive in the cement and dentin); and type VII—mixed fracture (cohesive in the cement and hybrid layer).

Interfacial micromorphology of the resin cements to dentin

Nine third molars were selected and sectioned to obtain 1.5 ± 0.5 mm thick dentin disks. To obtain these disks, teeth were perpendicularly sectioned along the long axis, exposing the middle dentin. Two disks of each specimen were obtained to perform the cementation procedures. Only the occlusal side of the apical slice was used for bonding, and thus pulp chamber exposure was not considered a relevant problem. The exposed dentin surfaces were wet-polished with #600-grit SiC paper (Buehler) to create a standardized smear layer.[18] Cementation procedures followed the protocol in accordance with the experimental groups previously described. Each pair of dentin disks cemented was sectioned using a slow-speed water-cooled diamond saw to obtain four bonding regions. Specimens were embedded in epoxy resin (Castin' Craft Clear Liquid Plastic, Environmental Technology, Fields Landing, CA), manually wet-sanded with #1200-grit SiC paper (Buehler) and polished using 6-, 3-, 1-, and 0.25-μm diamond pastes (Metadi II, Buehler) with wet felt disks.

After polishing, specimens were superficially demineralized with 50% phosphoric acid for 4 seconds. Then specimens were ultrasonically cleaned for 10 minutes in distilled water and subsequently immersed in a 1% sodium hypochlorite solution for 10 minutes.[20,21] To chemically dry the specimens, a dehydration process was also performed in ascending concentrations of ethanol (25%, 50%, 75%, 95%, and 100% for at least 20 minutes in each concentration) and immersed in hexamethyldisilazane (HMDS) for 10 minutes.[22] Specimens were then sputter coated with gold/palladium (SCD 050) and examined with SEM (JEOL-5600 LV) at 15 kV.

To complement the interfacial micromorphology analysis of RelyX Unicem to dentin, a specific specimen preparation was performed. In this case, each pair of dentin disks cemented was cleavage fractured using a steel blade at room temperature. This technique was performed at this temperature, since RelyX Unicem presents no adhesive layer at the interface. As this low-modulus layer is not present, no plastic deformation as a result of the cleavage is generated. The exposed bonding interfaces were neither embedded in epoxy resin nor polished. Fractured specimens were water-rinsed, and the excess water

Table 2 Protocol of the procedures used to cement indirect restoration

Groups	Dentin conditioning	Luting procedures
All-Bond 2 + C&B Cement	Etching with phosphoric acid gel (32%) for 15 seconds; water rinsing and drying with absorbing paper; application of 2 layers of the mixture of primer A and B; solvent evaporation for 5 seconds, no photoactivation, and application of the pre-bond resin adhesive	Mixing equal amounts of base and catalyst for 10 seconds; application to the dentin tissue and internal surface of restoration; indirect restoration slowly seated; remove excess; wait 7 minutes
Adper Single Bond 2 + RelyX ARC	Etching with phosphoric acid gel (37%) for 15 seconds; water rinsing and drying with absorbing paper; application of 2 layers of adhesive; solvent evaporation for 5 seconds and photoactivation for 10 seconds	Mixing equal amounts of base and catalyst for 15 seconds. Application of the cement to the dentin tissue and to the internal surface of restoration; indirect restoration slowly seated; remove excess; light-cure for 40 seconds all bonded surfaces
RelyX Unicem	No etching	Capsule activation for 2 seconds and mixing for 15 seconds using a high-frequency mixer device (Ultramat 2—SDI); application of resin cement to tooth surface and to the internal surface of restoration; indirect restoration slowly seated; remove excess; light-cure for 20 seconds all bonded surfaces

was removed using absorbent paper tissue. Specimens were then desiccated in silica gel for 12 hours. The specimens were subsequently coated with gold/palladium (SCD 050) and analyzed by SEM (JEOL-5600 LV). Particularly, an acceleration voltage at 20 kV was used for imaging the fractured specimens to obtain better-quality, high resolution images.

Table 3 Microtensile bond strength mean values in MPa (standard deviation) of experimental groups

	Storage time	
Resin cements	24 hours	30 days
C&B Cement/All-Bond 2	19.5 (3.8) C, a	24.5 (5.1) B, b
RelyX ARC/Adper Single Bond 2	40.8 (9.4) A, a	44.2 (8.5) A, a
RelyX Unicem	31.3 (7.4) B, a	28.3 (7.1) B, a

n = 5.
Within the same column, different uppercase letter: significant ($p < 0.05$).
Within the same row, different lowercase letter: significant ($p < 0.05$).

Results

The bond strength values are presented in Table 3. At the 24-hour evaluation, RelyX ARC/Adper Single Bond 2 presented significantly higher bond strength values than those obtained with RelyX Unicem and C&B Cement/All-Bond 2. Significance was also observed when RelyX Unicem was compared to the values for C&B Cement/All-Bond 2. After 30 days of water storage, bond strength values seen for RelyX ARC increased to 44.2 MPa, but no significance was seen in comparison to the mean values of the same group at the 24-hour evaluation. Statistical analysis also showed that the bond strength values for C&B Cement significantly increased after 30 days. RelyX Unicem presented statistically equivalent mean values after 30 days.

The failure pattern distribution (%) as analyzed by SEM can be observed in Figure 1. C&B Cement fracture analysis showed a prevalence of type II fracture pattern (cohesive fracture in the hybrid layer), independent of the storage time. For RelyX ARC, a higher percentage of type III fracture pattern (mixed fracture) was observed at the 24-hour and 30-day evaluation times. RelyX Unicem cement presented the highest percentages of type I fracture pattern (cohesive fracture in the cement) at both evaluation times. The percentage of type I fracture pattern increased for all three cements after 30 days.

Figures 2 to 4 provide examples of the fractographic analysis. Figures 2A and B illustrate a type I fracture pattern for RelyX Unicem. Higher magnifications (Figs 2C, D) highlight the morphologic aspect of the self-adhesive resin cement. No porosities are seen in this area of cohesive fracture. A dense resin organic matrix into which the inorganic particles are incorporated was observed. Fractographic illustrations of RelyX ARC are demonstrated in Figure 3. Figure 3A illustrates the type III mode of fracture. At a higher magnification (Fig 3B), the morphologic aspect of this type of fracture is highlighted, and the fractured components (adhesive, resin cement, and hybrid layer) are patent. Figure 3C exhibits the morphologic aspect of the cohesive fracture in the cement, represented by a nonporous dense tri-dimensional network of the resin cement matrix. In Figure 3D, it is possible to see a cohesive fracture in the hybrid layer where opened/sealed dentinal tubules coexist (black arrows).

The prevalent type II fracture pattern for C&B Cement is illustrated in Figure 4. Figures 4A and B show a general view of this mode of fracture. A higher magnification emphasizes the cohesive fracture in the hybrid layer with the presence

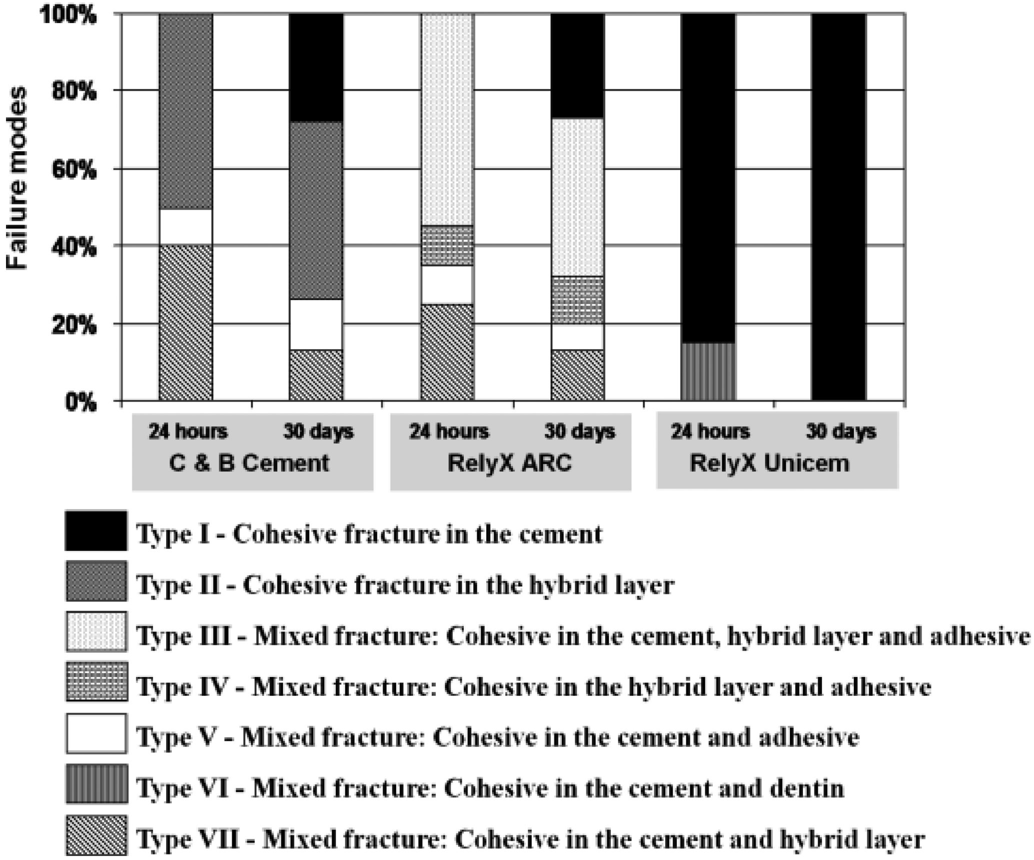

Figure 1 Proportional prevalence of failure modes after microtensile bond strength testing for all experimental groups after 24 hours and 30 days.

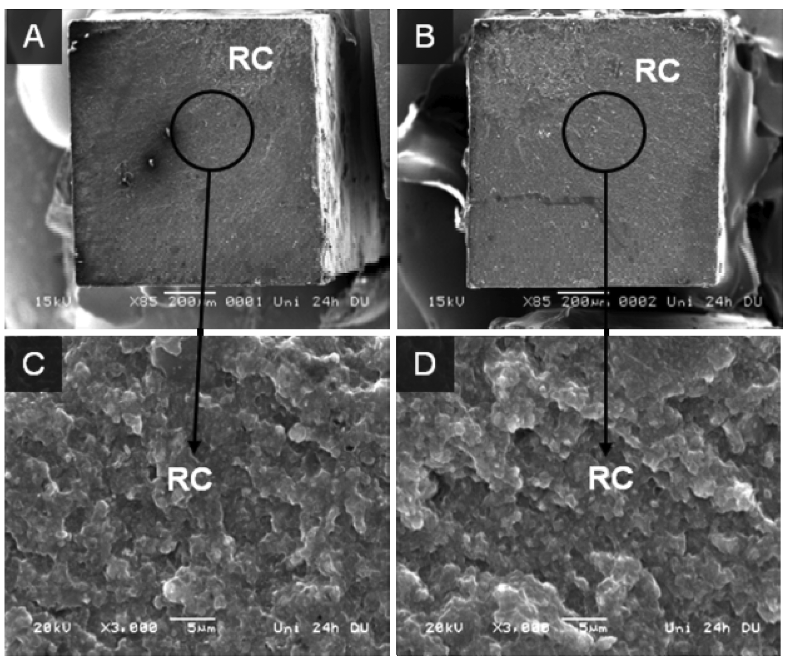

Figure 2 Photomicrography images of RelyX Unicem at 24-hour evaluation time. In A and B, opposite sides of a fractured specimen illustrate type I fracture pattern (85×). C and D represent the circled regions in A and B at higher magnification. The morphological aspect of a fractured region of the RelyX Unicem cement, in which a dense resin matrix with no porosity involving the inorganic fillers, is observed. The characteristic morphology is demonstrated (3000×). RC—resin cement.

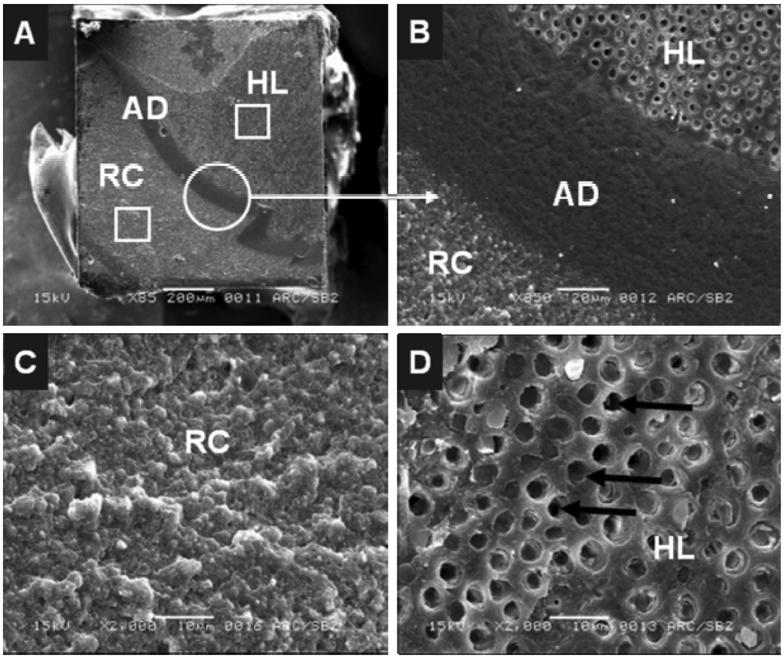

Figure 3 SEM fractography analysis of RelyX ARC/Adper Single Bond 2 (30 days). In A, the type III fracture pattern can be seen (at 85×). B exhibits the circled region in A at higher magnification (mixed fracture into the adhesive, resin cement, and hybrid layer) (at 850×). C shows the squared regions in A at higher magnification: a dense resin matrix illustrates the morphologic aspect after cohesive fracture of the resin cement; and D: a cohesive fracture in the hybrid layer is noticed, where both opened and obstructed dentin tubules (black arrows) are also observed (2000×). AD—adhesive; RC—resin cement; HL—hybrid layer.

of opened/sealed dentinal tubules (Fig 4C) and some fractured resin tags on the correspondent resin side of the fracture (Fig 4D).

Figures 5 and 6 illustrate the interfacial micromorphology of the resin cements to dentin. Different representations of the interfacial micromorphology formed by RelyX Unicem are demonstrated in Figure 5. In Figures 5A and B, in which the specimens were fractured to be microscopically analyzed, the intimacy of the contact dentin/resin cement is demonstrated. Resin tags in the dentin tubules are seen at short extensions. In Figures 5C and D, in which the specimens received the complete preparation process, it is possible to notice the interfacial micromorphology in which neither the hybridization zone nor the resin tags are evident. Only a tenuous brighter area at the bonding region, caused by an edging effect, was observed. On the other hand, the combination of RelyX ARC/Adper

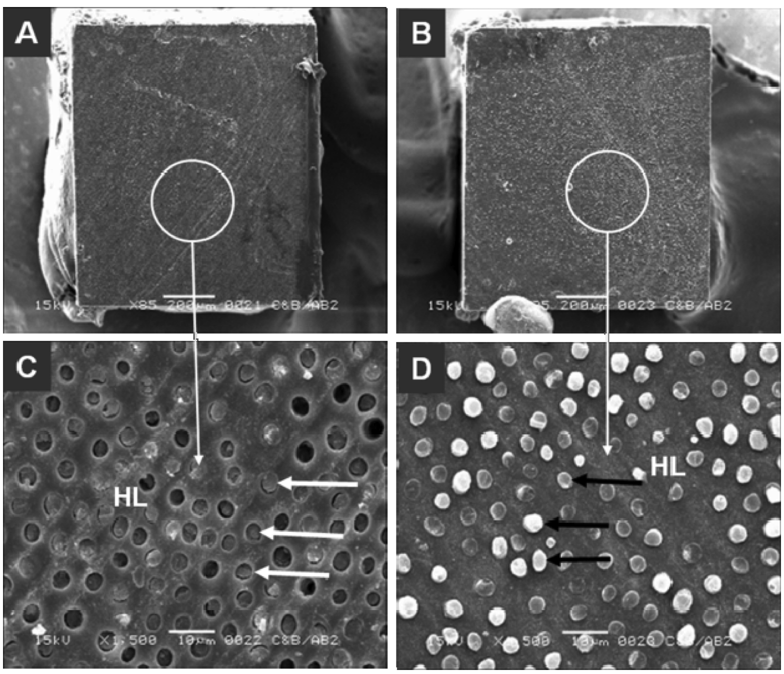

Figure 4 SEM fractography analysis of C&B Cement/All-Bond 2 (24 hours). In A and B, opposite sides of the same fractured specimen are observed, illustrating type II fracture pattern (85×). C and D present, at higher magnification, images of the circled areas in A and B, the morphologic aspect of the cohesive fracture in the hybrid layer (HL), precluded dentin tubules (white arrows) and fractured fragments of the resin extensions (black arrows) can be observed (at 1500×).

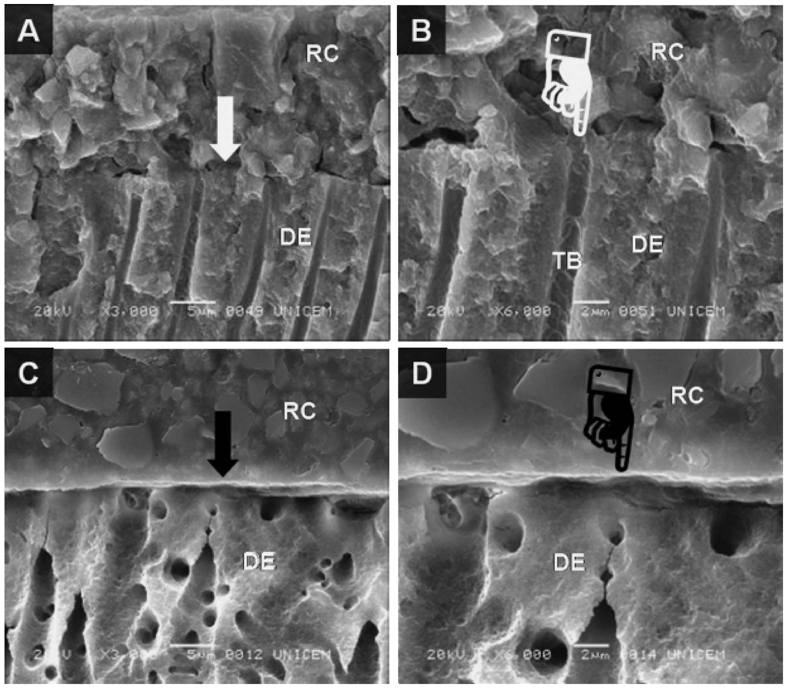

Figure 5 SEM photomicrograph of RelyX Unicem bonded to dentin. A (3000×) and B (6000×) (fractured specimens) exhibit an intimate contact of the resin cement with the dentin tissue (white arrow); dentin tubules (TB) with no resin infiltration (white hand) were noticed. In C and D (conventionally processed specimens), images show a non-authentic hybrid layer (black arrow) and also the interaction between the resin cement and the dentin (black hand). RC—resin cement; DE—dentin.

Single Bond 2 exhibited a typical hybrid layer, continuous and homogeneous with the presence of resin tags (Figs 6A, B). The interfacial micromorphology provided by the combination C&B Cement/All-Bond 2 exhibited an irregular hybrid layer in which a granular aspect is observed, associated with extended resin tags (Figs 6C, D).

Discussion

The research hypothesis, which held that there would be no difference in the bond strength when commercial resin cements were used to cement indirect composite restorations, regardless the evaluation time, was not validated. Statistical analysis

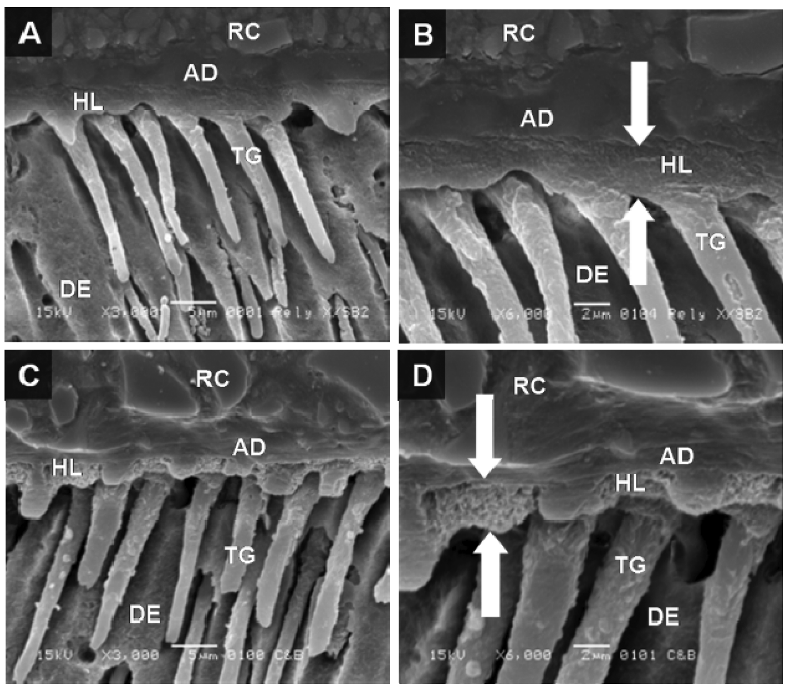

Figure 6 SEM photomicrograph of the interfacial micromorphology of different resin cements. A (3000×) and B (6000×): representative area of the resin/dentin interface of RelyX ARC/Adper Single Bond 2 showing a uniform hybrid layer of 4 to 6 μm in thickness (HL—between arrows). C and D: representative area of the resin/dentin interface of C&B Cement/All-Bond 2, showing a hybrid layer of 3 to 4 μm in thickness (HL—between arrows) in which a granular aspect is observed as a result of micro-spaces. RC—resin cement; DE—dentin; TG—resin tags (funnel shape); AD—adhesive layer.

revealed significantly higher mean bond strength values at the 24-hour evaluation time when both dual-cured cements (RelyX ARC, RelyX Unicem) were applied ($p < 0.05$). After 30 days, a significant increase in the bond strength was observed for the auto-cured C&B Cement ($p < 0.05$). At that time, values obtained for RelyX Unicem were statistically equivalent compared to the values of the C&B Cement.

The explanation of the increased bond strength values for C&B Cement seems to be related to its polymerization process. Specimens were tested after 30 days, a time after which the resin cement chemically completed its polymerization,[23] rendering the bonding region physically more resistant to tensile forces. The interfacial micromorphology of the bonding region formed by C&B Cement helps to clarify the higher incidence of the type II fracture pattern at both evaluation times. An irregular hybrid layer with a granular aspect can be mostly seen for the auto-cured cement (Figs 6C, D). The micro-spaces observed in the hybrid layer might be explained as a function of the solvent contained in the All-Bond 2 adhesive system. This bonding agent contains acetone as a solvent, which presents higher vapor pressure (184 mm Hg at 20°C) compared with ethanol (43.9 mm Hg) and water (17.5 mm Hg).[24] The acetone-based adhesives normally present a lower monomer-solvent ratio,[25] which would require the application of an increased number of layers to achieve the same amount of monomers to form an adequate bonding interface. As the same application protocol was used for both adhesives (application of two layers of adhesive system), the amount of monomers available for hybrid layer formation was lower for All-Bond 2. This is probably the main factor responsible for the granular aspect of the hybrid layer exhibited by the interaction of this adhesive system with etched dentin. Possibly, the application of increased number of layers of the adhesive All-Bond 2 would provide a more homogeneous hybrid layer. For this reason, the hybrid layer was supposed to represent the weakest link when the bonding region was submitted to tensile forces.

According to the manufacturer's instructions, primers A and B of bonding agent All-Bond 2 need to be mixed and applied to the dentin tissue after the acid-etching procedure. A pre-bonding resin is then applied over this layer. This resin contains benzoyl peroxide, which favors the tertiary amine contained in the catalyst paste of C&B Cement to start the chemical polymerization reaction. In the present study, All-Bond 2 primers were not photoactivated after the application on the dentin. This recommendation is usually made to clinicians when they are cementing a dowel to the root canal. Based on the results of a previous study,[26] higher bond strength mean values are obtained when the mixture of primers is applied and not photoactivated. An unpolymerized mixture of primers A and B (which contains the photoinitiators) favors the reaction with the pre-bond resin, which contains hydrophobic and BHT (2.6-di-tec-butil-p-hidroxi toluene) monomers (polymerization inhibitor). The photoactivation of the primers would reduce the amount of NTG-GMA (N-2-hidroxi-3-methacriloiloxipropil-N-fenilglicine), contained in primer A, available to react. This component is known to function as an accelerator of the autocure reaction.[26] Also, if the mixture of primers A and B was polymerized, a greater amount of BHT monomer contained in the pre-bond resin would be available to react with the resin cement. In this case, the increased amount of free BHT monomers would partially inhibit the chemical polymerization reaction of the resin cement, and a decrease in the bond strength values might occur.

Combination RelyX ARC/Adper Single Bond 2 presented significantly higher bond strength mean values at both evaluation times compared to the values provided by the auto-cured cement (C&B Cement). These results can be partially explained in the function of the mechanical properties of the resin cement. In a previous study,[27] in which the degree of conversion of various resin cements was evaluated in different cure circumstances, RelyX ARC achieved the maximum conversion value when this cement was light-cured. Clinically, immediate photoactivation of the marginal cement after seating an indirect restoration is recommended to avoid premature crown removal. The polymerization completion at internal areas not reached by energy provided by the curing light occurs through chemical reaction, which takes about 24 hours (manufacturer's information). Complete cement polymerization is of paramount importance for achieving adequate bond strength and increased mechanical properties. The quality of polymerization and the stiffness of the cement are considered substantial factors that may affect the interfacial performance of a luting agent.[28]

The magnitude of the bond strength values provided to the RelyX ARC resin cement was also influenced by the quality of the hybrid layer formed with the application of Adper Single Bond 2. The morphologic analysis showed an evident and homogeneous hybrid layer with the presence of resin tags (Figs 6A, B). The ability of the adhesive monomers to envelop the collagen fibrils is dependent on many factors including: conditioning and priming steps, specific wetting characteristics of the adhesives, the chemical composition,[29] especially concerning the hydrophilic/hydrophobic nature of the resins,[30] and the individual monomer property.[31] Another important factor responsible for the homogeneous aspect of the hybrid layer produced by the application of Adper Single Bond 2 is the presence of ethanol as a solvent, which makes it less critical to form imperfections in the hybrid layer when compared to acetone-based materials.[25] Moreover, it contains 10% by weight of silica nanofillers (5 nm).[32,33] These particles are displayed in a uniform and continuous layer after the polymerization process. The amount of silica particles contained in the adhesive system does not increase its viscosity and helps decrease the reaction of camphorquinone radicals with oxygen molecules to form non-reactive peroxyradicals that inhibit the polymerization reaction.[34] Thus, when the resin cement is applied to the polymerized adhesive surface, a net of free radicals from the resin cement diffuses into the adhesive, increasing the monomer conversion at the adhesive/resin cement contact area during the photoactivation. This is why after 30 days, despite the statistical equivalence in the bond strength values, an increase in the mean bond strength values was noticed (from 40.8 ± 9.4 to 44.2 ± 8.5 MPa) for RelyX ARC/Adper Single Bond 2. On the other hand, an increase in the percentage of cohesive failures in the cement was observed (from 0 to 25%).

Resin cements relying on the use of etch-and-rinse adhesives achieved higher bond strength values with a characteristic hybrid layer. Considering that a conventional two-step, etch-and-rinse adhesive is used in association with RelyX ARC and the possibility of chemical incompatibility as a result of this association,[11] one can speculate that this factor may impart short-term longevity to the restoration; however, results seen in the present study do not corroborate these previous findings. The bond strength to dentin seen when this resin cement was applied was of the same magnitude after 30 days of water storage, and the fracture pattern did not exhibit evidence of incompatible reaction. This might be explained because the photoactivation procedure was immediately performed, thus not providing enough time for the incompatibility reaction to occur.

Significantly higher bond strength values were found when RelyX Unicem was applied compared to the values obtained with C&B Cement at the 24-hour evaluation time. After 30 days, a statistical equivalence occurred between the mean bond strength values obtained using these cements. At the 24-hour evaluation time, the majority of fractures for RelyX Unicem were cohesive in the cement. After 30 days, all fractures were cohesive in the cement. One may argue that those bond strength values actually represent the cohesive resistance of the cement rather than the magnitude of the bonding of the material to the dentin tissue. Fractographic analysis demonstrated the morphology of the fractured area with the presence of irregular but nonporous compacted resin matrix where inorganic particles are incorporated (Fig 2). In a different way from that seen for combinations RelyX ARC/Adper Single Bond 2 and C&B Cement/All-Bond 2, the interfacial micromorphology of RelyX Unicem revealed a thin "hybrid-like layer" (Fig 5). Monticelli et al[35] pointed out that no hybrid layer or resin tags were detected in the interfaces formed when RelyX Unicem was applied. Results described in a previous study[36] using SEM microscopic analysis indicated that the indirect restorations cemented with RelyX Unicem presented an increased bond strength if a seating force greater than finger pressure was maintained throughout the initial settings of the cement. According to these authors, this might have contributed to the reduction in the film thickness and porosity of this cement. Another study[12] reported that RelyX Unicem interacted superficially with the dental tissues, and the thickness ranged between 0 and 2 μm. Based on this information, the authors speculated that this width actually corresponded to irregularities of the smear layer produced by the clinicians during preparation, which explains the absence of hybrid layer and resin tags. Thus, the hypothesis raised in that study that the bonding mechanism of RelyX Unicem is similar to those obtained with auto-conditioning systems was proven not valid. In this case, the weakest link would be the resulting reaction between the smear layer and the underlying intact mineralized dentin,[10] findings not confirmed in the present study. Micromorphologic evaluation demonstrated that thanks to the intimacy exhibited by the self-adhesive cement, the majority of the fractures after testing were cohesive in the cement when RelyX Unicem was applied.

The clinical procedure for cementing indirect restorations when using a self-adhesive cement was simplified by the elimination of the pre-treatment step.[14] The bonding mechanism of the RelyX Unicem to the dentin tissue starts with the ionization of methacrylated phosphoric acid during the mixture of the monomers. Negatively charged phosphoric acid groups of methacrylate monomers react with calcium, incorporating the smear layer and bonding to the dental tissues. According to the manufacturer, the initial low acidity of the cement is then quickly neutralized during the polymerization process because the phosphoric acid groups also react with alkaline fillers.[15] Because of this reaction, mechanical properties of the cement are also enhanced. Studies have claimed that the low initial pH observed after mixing was insufficient to produce demineralization effects. As a consequence, there is no distinct demineralization and hybridization zone, which is commonly observed even with mild self-etching systems.[10,12] According to Hiraishi et al,[10] this self-adhesive cement required a relatively dry dentin surface, which in terms of the moisture contamination, might interfere with the bonding of the cement, reducing the bond strength values.[10] Conversely, the manufacturer claims this material has a higher moisture tolerance than do conventional luting cements. It has been considered that water storage can result in hydrolytic degradation of the chemical components of the resin cements at the interface. In general, the penetration of water molecules into the bonding area occurs due to the incomplete penetration of the adhesive into the demineralized zone or as a result of insufficient polymerization of the adhesive.[37] In this case, because the use of RelyX Unicem self-adhesive resin cement requires only one step, the need for steps such as etching, priming, and bonding are eliminated. In addition, since the dentin is not previously etched when RelyX Unicem is used, the smear layer is not removed, and the dentin tubules remain protected. Thus, technique-sensitive steps that include the need for moist dentin are not a problem for the self-adhesive cement.

The findings observed in the present investigation showed that the resin cements evaluated produce characteristic interfacial micromorphologies due to their particular interaction with dentin. Different formulations and application techniques also contributed to the bond strength of resin cements to dentin after 24 hours and 30 days of water storage. The acidic monomers incorporated in the self-adhesive cement were not strong enough to etch through smear layers to form an authentic hybrid layer along the interface. Despite the lower mean bond strength values compared to those produced with RelyX ARC, the self-adhesive cement produced statistically equivalent values and fracture patterns after 30 days of water storage.

Clinically, longevity depends on the numerous steps before restoration is completed. Simplification is critical for a successful restorative procedure, since many aspects need to be considered. A recent study[38] evaluated the clinical performance of indirect restorations after using RelyX Unicem for 2 years. The authors found acceptable clinical behavior in terms of marginal integrity, among other parameters. Even though self-adhesive cements certainly represent an evolving technology in indirect restorative procedures, studies are necessary to evaluate the longevity of indirect restorations cemented with this category of resin cement over longer evaluation times.

Conclusions

Within the limitations defined in the experimental design, the following conclusions may be drawn:

(1) The highest bond strength values were observed when the conventional dual-cured cement was applied, irrespective of evaluation time.
(2) The bonding to dentin of the dual-cured self-adhesive resin cement was comparable to that observed when a self-cured etch-and-rinse cement was applied.
(3) The interfacial micromorphology of cements associated with etch-and-rinse adhesives exhibited an authentic hybrid layer with resin tags, whereas the self-adhesive cement revealed only a tenuous interaction zone.
(4) Despite the absence of an authentic hybrid layer, the self-adhesive cement tested was able to promote adhesion with the underlying dentin.

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References

1. Pereira SG, Fulgencio R, Nunes TG, et al: Effect of curing protocol on the polymerization of dual-cured resin cements. Dent Mater 2010;26:710-718
2. Piwowarczyk A, Bender R, Ottl P, et al: Long-term bond between dual-polymerizing cementing agents and human hard dental tissue. Dent Mater 2007;23:211-217
3. Kumbuloglu O, Lassila LV, User A, et al: A study of the physical and chemical properties of four resin composite luting cements. Int J Prosthodont 2004;17:357-363
4. Attar N, Tam LE, McComb D: Mechanical and physical properties of contemporary dental luting agents. J Prosthet Dent 2003;89:127-134
5. de Souza Costa CA, Hebling J, Randall RC: Human pulp response to resin cements used to bond inlay restorations. Dent Mater 2006;22:954-962
6. Burrow MF, Nikaido T, Satoh M, et al: Early bonding of resin cements to dentin–effect of bonding environment. Oper Dent 1996;21:196-202
7. Pegoraro TA, da Silva NR, Carvalho RM: Cements for use in esthetic dentistry. Dent Clin North Am 2007;51:453-471
8. Carvalho RM, Pegoraro TA, Tay FR, et al: Adhesive permeability affects coupling of resin cements that utilise self-etching primers to dentine. J Dent 2004;32:55-65
9. Saskalauskaite E, Tam LE, McComb D: Flexural strength, elastic modulus, and pH profile of self-etch resin luting cements. J Prosthodont 2008;17:262-268
10. Hiraishi N, Yiu CK, King NM, et al: Effect of 2% chlorhexidine on dentin microtensile bond strengths and nanoleakage of luting cements. J Dent 2009;37:440-448
11. Sanares AM, Itthagarun A, King NM, et al: Adverse surface interactions between one-bottle light-cured adhesives and chemical-cured composites. Dent Mater 2001;17:542-556
12. De Munck J, Vargas M, Van Landuyt K, et al: Bonding of an auto-adhesive luting material to enamel and dentin. Dent Mater 2004;20:963-971
13. Kious AR, Roberts HW, Brackett WW: Film thicknesses of recently introduced luting cements. J Prosthet Dent 2009;101:189-192
14. Gerth HU, Dammaschke T, Zuchner H, et al: Chemical analysis and bonding reaction of RelyX Unicem and Bifix composites—a comparative study. Dent Mater 2006;22:934-941
15. Radovic I, Monticelli F, Goracci C, et al: Self-adhesive resin cements: a literature review. J Adhes Dent 2008;10:251-258
16. Pashley DH, Carvalho RM, Sano H, et al: The microtensile bond test: a review. J Adhes Dent 1999;1:299-309
17. Reis A, Loguercio AD, Azevedo CL, et al: Moisture spectrum of demineralized dentin for adhesive systems with different solvent bases. J Adhes Dent 2003;5:183-192
18. Pashley DH, Tao L, Boyd L, et al: Scanning electron microscopy of the substructure of smear layers in human dentine. Arch Oral Biol 1988;33:265-270
19. Shinohara MS, De Goes MF, Schneider LF, et al: Fluoride-containing adhesive: durability on dentin bonding. Dent Mater 2009;25:1383-1391
20. Montes MA, de Goes MF, da Cunha MR, et al: A morphological and tensile bond strength evaluation of an unfilled adhesive with low-viscosity composites and a filled adhesive in one and two coats. J Dent 2001;29:435-441
21. Duarte RM, de Goes MF, Montes MA: Effect of time on tensile bond strength of resin cement bonded to dentine and low-viscosity composite. J Dent 2006;34:52-61
22. Perdigao J, Lambrechts P, Van Meerbeek B, et al: Field emission SEM comparison of four postfixation drying techniques for human dentin. J Biomed Mater Res 1995;29:1111-1120
23. Venhoven BA, de Gee AJ, Davidson CL: Light initiation of dental resins: dynamics of the polymerization. Biomaterials 1996;17:2313-2318
24. Gallo JR, Burgess JO, Xu X: Effect of delayed application on shear bond strength of four fifth-generation bonding systems. Oper Dent 2001;26:48-51
25. Reis AF, Oliveira MT, Giannini M, et al: The effect of organic solvents on one-bottle adhesives' bond strength to enamel and dentin. Oper Dent 2003;28:700-706
26. Swift Jr. EJ, May Jr. KN, Wilder Jr. AD: Effect of polymerization mode on bond strengths of resin adhesive/cement systems. J Prosthodont 1998;7:256-260
27. Arrais CA, Giannini M, Rueggeberg FA: Kinetic analysis of monomer conversion in auto- and dual-polymerizing modes of commercial resin luting cements. J Prosthet Dent 2009;101:128-136
28. Al-Assaf K, Chakmakchi M, Palaghias G, et al: Interfacial characteristics of adhesive luting resins and composites with dentine. Dent Mater 2007;23:829-839
29. Perdigao J, Ramos JC, Lambrechts P: *In vitro* interfacial relationship between human dentin and one-bottle dental adhesives. Dent Mater 1997;13:218-227
30. Wang Y, Spencer P: Evaluation of the interface between one-bottle adhesive systems and dentin by Goldner's trichrome. Am J Dent 2005;18:66-72
31. Pioch T, Staehle HJ, Duschner H, et al: Nanoleakage at the composite-dentin interface: a review. Am J Dent 2001;14:252-258
32. Rodrigues Jr. SA, Ferracane JL, Della Bona A: Influence of surface treatments on the bond strength of repaired resin composite restorative materials. Dent Mater 2009;25:442-451
33. Erickson RL, Barkmeier WW, Kimmes NS: Fatigue of enamel bonds with self-etch adhesives. Dent Mater 2009;25:716-720

34. Rueggeberg FA, Margeson DH: The effect of oxygen inhibition on an unfilled/filled composite system. J Dent Res 1990;69:1652-1658
35. Monticelli F, Osorio R, Mazzitelli C, et al: Limited decalcification/diffusion of self-adhesive cements into dentin. J Dent Res 2008;87:974-979
36. Goracci C, Cury AH, Cantoro A, et al: Microtensile bond strength and interfacial properties of self-etching and self-adhesive resin cements used to lute composite onlays under different seating forces. J Adhes Dent 2006;8:327-335
37. De Munck J, Van Landuyt K, Peumans M, et al: A critical review of the durability of adhesion to tooth tissue: methods and results. J Dent Res 2005;84:118-132
38. Peumans M, De Munck J, Van Landuyt K, et al: Two-year clinical evaluation of a self-adhesive luting agent for ceramic inlays. J Adhes Dent 2010;12:151-161