Effects of a Peripheral Enamel Margin on the Long-term Bond Strength and Nanoleakage of Composite/Dentin Interfaces Produced by Self-adhesive and Conventional Resin Cements

Alline C. Kasaz[a] / Carlos E. Pena[b] / Rodrigo S. de Alexandre[c] / Ronaldo G. Viotti[d] / Veronica B. Santana[e] / Cesar A. G. Arrais[f] / Marcelo Giannini[g] / Andre F. Reis[h]

Purpose: This study evaluated the effects of peripheral enamel margins on the long-term bond strength (µTBS) and nanoleakage in resin/dentin interfaces produced by self-adhesive and conventional resin cements.

Materials and Methods: Five self-adhesive [RelyX-Unicem (UN), RelyX-U100 (UC), GCem (GC), Maxcem (MC), Set (SET)] and 2 conventional resin cements [RelyX-ARC(RX), Panavia F(PF)] were used. An additional group included the use of a two-step self-etching adhesive (SE Bond) with Panavia F (PS). One hundred ninety-two molars were assigned to 8 groups according to luting material. Five-mm-thick composite disks were cemented and assigned to 3 subgroups according to water-exposure condition (n = 6): 24-h peripheral exposure (24h-PE-enamel margins), or 1 year of peripheral (1yr-PE) or direct exposure (1yr-DE-dentin margin). Restored teeth were sectioned into beams and tested in tension at 1 mm/min. Data were analyzed by two-way ANOVA and Tukey's test. Two additional specimens in each group were prepared for nanoleakage evaluation. Nanoleakage patterns were observed under SEM/TEM.

Results: Except for RX, no significant reduction in µTBS was observed between 24h-PE and 1yr-PE. 1yr-DE reduced µTBS for RX, PF, GC, MC, and SET. No significant reduction in µTBS was observed for PS, UC, and UN after 1 year. After 1yr-DE, RX and PS presented the highest µTBS, and SET and MC the lowest. Nanoleakage was reduced when there was a peripheral enamel margin. SET and MC presented more silver deposition than other groups.

Conclusion: The presence of a peripheral enamel margin reduced the degradation rate in resin/dentin interfaces for most materials. The µTBS values produced by the multi-step luting agents RX and PS were significantly higher than those observed for self-adhesive cement

Keywords: self-adhesive cements, resin cements, TEM, SEM, nanoleakage, microtensile bond strength.

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[a] *Master's Student, Department of Restorative Dentistry, Guarulhos University, Guarulhos, SP, Brazil. Performed the experiments in partial fulfillment of requirements for Master's degree in Restorative Dentistry.*

[b] *PhD Student, Department of Restorative Dentistry, Guarulhos University, Guarulhos, SP, Brazil. Contributed to the TEM and SEM specimen preparation procedures.*

[c] *PhD Student, Department of Restorative Dentistry, Guarulhos University, Guarulhos, SP, Brazil. Contributed to the microtensile bond strength procedures.*

[d] *PhD Student, Department of Restorative Dentistry, Guarulhos University, Guarulhos, SP, Brazil / Blumenau Regional University, Blumenau, SC, Brazil. Performed cementation of indirect composite restorations.*

[e] *Master's Student, Department of Restorative Dentistry, Guarulhos University, Guarulhos, SP, Brazil. Contributed to the microtensile bond strength procedures.*

[f] *Assistant Professor, Department of Restorative Dentistry, Guarulhos University, Guarulhos, SP, Brazil. Performed statistical evaluation.*

[g] *Associate Professor, Department of Restorative Dentistry, Piracicaba School of Dentistry, University of Campinas, Piracicaba, SP, Brazil. Contributed substantially to discussion.*

[h] *Assistant Professor, Department of Restorative Dentistry, Guarulhos University, Guarulhos, SP, Brazil. Developed experimental design, performed TEM analysis and wrote manuscript.*

Correspondence: *Dr. Andre F. Reis, Department of Restorative Dentistry, Guarulhos University, Praça Tereza Cristina, 229, Centro, Guarulhos, SP, Brazil CEP 07023-070. Tel/Fax: +55-11-2464-1758. e-mail: areis@prof.ung.br*

Bonding of resin-based composite materials to dental hard tissues has been simplified in recent years. A few years ago, most adhesives were available in three application steps, which were combined into two steps (etch-and-rinse or self-etching) and later, in one single self-etching application step. Indirect adhesive procedures constitute a substantial portion of esthetic restorative procedures. Until recently, all resin cements required the application of one of these adhesive systems, either self-etching or etch-and-rinse, to prepare the tooth prior to cementation.[6,14] However, the multi-step application technique has been reported to be complex and technique sensitive, and can compromise bonding effectiveness.[9]

A new concept of luting materials has been recently developed which does not require any pretreatment of the tooth surface: the so-called self-adhesive cements.[1,3,12] These materials aim to combine the favorable properties of traditional (zinc-phosphate, glass-ionomer and polycarboxylate cements) and conventional resin cements, eliminating their shortcomings.[18] After the first self-adhesive cement was introduced, it rapidly gained popularity among clinicians due to its simplified application technique.

A wide variety of self-adhesive cements are currently available on the market, but only limited information is available with regard to the long-term bond strength and sealing ability of the interfaces produced by the self-adhesive systems.[6,10,18,19] The ability of some self-adhesive cements to demineralize and infiltrate smear-layer covered dentin has been questioned.[12,16,23]

It is well known that bond strength and sealing integrity produced by bonding agents can decrease with time.[19] Water sorption within resin/dentin interfaces has been cited as one of the dominant factors involved in adhesion degradation.[4,11,21] Water sorption and the solubility of adhesive resin cements are important factors in determining the longevity and marginal integrity of an indirect restoration. It has been demonstrated that a composite-enamel bond adjacent to a composite-dentin bond might help protect the resin/dentin interface against degradation for some adhesive systems, as long as that peripheral bond remains intact.[7,20] Based on this evidence, it was hypothesized that a composite-enamel bond created by self-adhesive resin cements could also protect resin/dentin interfaces produced by these cements against degradation.

The purpose of this study was to evaluate changes in microtensile bond strength (μTBS) and nanoleakage patterns of self-adhesive and conventional resin cements after aging specimens in water for 1 year. Experimental conditions included specimen exposure to water either peripherally, in which specimens had an enamel-resin bond surrounding the restoration, or directly against dentin margins. The tested null hypotheses were that (1) there is no difference in the μTBS and nanoleakage patterns of composite/dentin interfaces produced by self-adhesive and conventional resin cements, and (2) the different conditions of water exposure do not affect the μTBS values or nanoleakage patterns of composite/dentin interfaces over one year.

MATERIALS AND METHODS

One hundred ninety-two recently extracted caries-free third molars stored in 0.1% thymol solution at 4°C were used. The teeth were obtained by a protocol approved by the review board of the Guarulhos University (#152/2007). Flat coronal dentin surfaces were exposed with 600-grit SiC papers under running water to create a standardized smear layer. The peripheral enamel was removed from the teeth in the experimental groups of direct water exposure with a diamond bur mounted in a high-speed handpiece under water cooling prior to the restorative procedures. The presence of a composite-enamel bond surrounding the restoration was classified as "peripheral", and the absence of enamel was classified as "direct".[7,20] Flattened teeth were randomly assigned to 3 experimental groups, according to the water exposure condition: 24 h of peripheral water exposure (24h-PE), one year of peripheral water exposure (1Yr-PE), or one year of direct water exposure (1Yr-DE).

Teeth were then assigned to 8 experimental subgroups, which were restored with one of the 8 luting techniques (n = 6). Five self-adhesive cements were used in the present study: RelyX Unicem ([UN], 3M ESPE; Seefeld, Germany), RelyX U100 ([UC], 3M ESPE; Seefeld, Germany), G-Cem ([GC], GC America; Alsip, IL, USA), Maxcem ([MC], Kerr; Orange, CA, USA) and Set ([SET], SDI; Bayswater, Victoria, AUS); and two conventional resin cements: one that uses a two-step etch-and-rinse adhesive (RelyX ARC [RX]), and one that uses a one-step self-etching adhesive (Panavia F [PF], Kuraray; Osaka, Japan). In order to test if a two-step self-etching system would perform better than a one-step self-etching adhesive, an additional group was made by using a two-step self-etching adhesive system (Clearfil SE Bond) prior to the application of Panavia F (PS). Resin cements were mixed and inserted according to manufacturers' instructions (Table 1).

Composite resin blocks of approximately 5 mm in height and 12 mm in diameter were prepared by layering 2-mm-thick increments of the microhybrid composite resin Z250 (shade A2, 3M ESPE) into a silicon mold. Each increment was light cured (650 mW/cm^2) for 40 s with a halogen light (Optilux 501, Demetron/Kerr; Danbury, CT, USA). One side of the composite resin blocks was abraded with #600 SiC paper under water cooling to create a flat surface with standardized roughness. The composite surface was air abraded with 50-μm aluminum oxide particles for 10 s. Before luting procedures, the composite resin blocks were ultrasonically cleaned in distilled water for 10 min, rinsed with running water, air dried, and silanated with RelyX Ceramic Primer (3M ESPE).

After application of the resin cement according to manufacturer's instructions, the composite block was seated using finger pressure, and the excess cement was removed with disposable microbrushes prior to polymerization. Specimens were light cured for 40 s from the buccal, lingual, and occlusal surfaces. Afterwards, excess

Table 1 Cements, lot number, manufacturers, delivery system, composition, and application technique

Type	Product [abbr.] (lot #), manufacturer	Delivery system (cement)	Composition	Application technique
Dual-curing resin cement + etch-and-rinse adhesive system	RelyX ARC [RX] (GEHG) + Adper Single Bond 2 (8RW) 3M ESPE; St Paul, MN, USA	Clicker dispenser, 2 paste hand mixed for 10 s	Etchant: 35% H_3PO_4 (8MR). Adhesive: bis-GMA, HEMA, UDMA, dimethacrylates, ethanol, water, camphorquinone, photoinitiators, polyalkenoic acid copolymer, 5-nm silica particles. Cement: bis-GMA, TEG-DMA, polymer, zirconia/silica filler.	a (15 s); b (15 s); c; d; e; i (10 s); mix cement; apply mixture
Dual-curing resin cement + one-step self-etching adhesive	Panavia F [PF] (paste A 00248C; paste B 0026B) + ED Primer (primer A 00255A; primer B 00131A) Kuraray Medical; Tokyo, Japan	One-step self-etching adhesive + resin cement dual-curing 2 paste/hand mixed	Primer A: HEMA, 10-MDP, 5-NMSA, water, accelerator. Primer B: 5-NMSA, accelerator, water, sodium benzene sulphinate. Paste A: 10-MDP, silanated silica, hydrophobic aromatic and aliphatic dimethacrylate, hydrophilic dimethacrylate photo-initiator, dibenzoyl peroxide. Paste B: silanated barium glass, sodium fluoride, sodium aromatic sulfinate, dimethacrylate monomer, BPO.	h (A+B) (leave undisturbed for 60 s); mix cement; apply mixture; i (40 s)
Dual-curing resin cement + two-step self-etching adhesive system	Panavia F + [PS] (paste A 00248C; paste B 0026B) + Clearfil SE Bond (00788A) Kuraray Medical	Two-step self-etching adhesive + ED primer + resin cement dual-curing 2 paste/hand mixed	Primer: MDP, HEMA, hydrophilic dimethacrylate, dl-camphorquinone, N,N-diethanol p-toluidine, water. Bond: MDP, bis-GMA, HEMA, hydrophobic dimethacrylate, dl-camphorquinone, N,N-diethanol p-toluidine, silanated colloidal silica. Paste A and Paste B: As described above.	f (20 s); e; g; i (10 s); h (ED primer); e; mix cement; apply mixture; i (40 s)
Dual-curing self-adhesive resin cement	G-CEM [GC] (0702191) GC America; Alsip, IL,USA	Capsules, mechanically mixed 10 s	Powder: fluoroaluminosilicate glass, initiator, pigment. Liquid: 4-META, phosphoric acid ester monomer, water, UDMA, dimethacrylate, silica powder, initiator, stabilizer.	Auto-mix cement, apply mixture; i (40 s) or j (5min)
Dual-curing self-adhesive resin cement	RelyX U100 [UC] (287269) 3M ESPE; Seefeld, Germany	Clicker dispenser 2 paste hand mixed	Base: methacrylate monomers containing phosphoric acid groups, methacrylate monomers, silanated fillers, initiator components, stabilizers. Catalyst: methacrylate monomers, alkaline fillers, silanated fillers, initiator components, stabilizers, pigments.	Mix cement, apply mixture; i (40 s) or j (5min)
Dual-curing self-adhesive resin cement	RelyX Unicem [UN] (293599) 3M ESPE; Seefeld, Germany	Capsules, mechanically mixed, 10 s	Powder: glass powder, silica, calcium hydroxide, self-curing initiators, pigments, light-curing initiators, substituted pyrimidine, peroxy compound. Liquid: methacrylated phosphoricesters, dimethacrylates, acetate, stabilizers, self-curing initiators, light-curing initiators.	Auto-mix cement, apply mixture, i (40 s) or j (5min)
Dual-curing self-adhesive resin cement	Maxcem [MC] (2954635) Kerr; Orange, CA, USA	Paste/paste dual syringe, direct dispensed through a mixing tip	Resin: multifunctional DMAs, GPDM, proprietary redox initiators and photoinitiators. Filler: barium, fluoroaluminosilicate, fumed silica (66 wt%).	Auto-mix cement, apply mixture; i (20 s) or j (3min)
Dual-curing self-adhesive resin cement	Set [SET] (50711292) SDI; Bayswater, Victoria, AUS	Capsules, mechanically mixed, 10 s	Methacrylated phosphoric esters, UDMA, photoinitiator 67 wt% (45 vol%), fluoroaluminosilicate glass, pyrogenic silica.	Auto-mix cement, apply mixture i (20 s) or j (5 min)

Application techniques: a: acid etch; b: rinse surface; c: dry with cotton pellet; d: apply one-bottle adhesive; e: gently air dry; f: apply primer; g: apply adhesive; h: apply mixture; i: light cure; j: self-cure.

cement was removed with extra-fine diamond burs on a high-speed handpiece. Bonded specimens were stored in distilled water for 24 h or 1 year. Afterwards, teeth were serially sectioned perpendicular to the adhesive/tooth interface into beams with a cross-sectional bonded area of approximately 1 mm^2 using a diamond saw (Isomet 1000, Buehler; Lake Bluff, IL, USA). Beams were fixed to the grips of a universal testing machine (EZ Test, Shimadzu; Kyoto, Japan) using a cyanoacrylate adhesive (Loctite Super Bonder Gel, Henkel; Düsseldorf, Germany) and tested in tension at a crosshead speed of 1 mm/min until fracture. Maximum tensile load was divided by specimen cross-sectional area to express results in units of stress (MPa).

Bond strength values were statistically evaluated using two-way ANOVA and the Tukey post-hoc test at a pre-set significance level of 0.05. Statistical analyses were performed using statistical software (SAS for Windows V9, SAS Institute; Cary, NC, USA). Pre-test failures were not included in the statistical analysis.

Failure modes were determined by examination of fractured specimens in a scanning electron microscope (LEO 435 VP, LEO Electron Microscopy; Cambridge, UK). Specimens were mounted on aluminum stubs and gold sputter coated (MED 010, BAL-TEC; Balzers, Liechtenstein) prior to viewing at different magnifications. Failure mode at the fractured interface was classified into one of four types: CD (cohesive failure in dentin), AD (adhesive failure between cement and dentin), CC (cohesive failure in the cement) and ADR (adhesive failure between the resin cement and composite resin). Instead of classifying failures as mixed, the percent area of each type of failure in each specimen was recorded.

Nanoleakage Evaluation

Two additional specimens in each group were prepared for nanoleakage evaluation. After resin cements were mixed and applied onto the flat dentin surfaces, a polyester strip was placed over the resin cement and a glass plate was used to apply proper digital pressure while the resin cement was light-cured for 40 s. Next, in order to facilitate ultrathin sectioning, a thin layer of a low-viscosity resin composite (Clearfil Protect Liner F, Kuraray Medical; Kurashiki, Japan; or Surefil SDR flow, Dentsply Caulk; Milford, DE, USA) was applied and light cured for 40 s. After each water storage period, the teeth were subjected to a silver impregnation protocol.

Bonded teeth were coated with two layers of nail varnish applied up to within 1 mm of the bonded interfaces. In order to rehydrate specimens and avoid desiccation artifacts,[2] they were immersed in distilled water for 20 min prior to immersion in ammoniacal silver nitrate for 24 h.[22] Tooth slabs were placed in the tracer solution in total darkness for 24 h, rinsed in distilled water, and immersed in a photodeveloping solution for 8 h under a fluorescent light to reduce silver ions into metallic silver grains within voids along the interface. Specimens were then sectioned into 0.9-mm-thick slabs and additionally photodeveloped for 8 h.

Transmission (TEM) and Scanning Electron Microscopy (SEM)

Specimens were examined with the TEM to compare silver uptake patterns along resin/dentin interfaces. Undemineralized specimens were fixed in Karnovsky's solution, post-fixed in osmium tetroxide, dehydrated in an ascending ethanol series, and embedded in epoxy resin (Dr. Spurr, Electron Microscopy Sciences; Hatfield, PA, USA). Representative 90-nm-thick ultrathin sections were prepared with an ultramicrotome (Leica UC6, Leica Microsystems; Wetzlar, Germany) and collected on 100-mesh copper grids. Without additional staining, they were observed in a TEM (Zeiss EM 900, Zeiss; Munich, Germany) operated at 80 KV. Silver deposition patterns were compared among the different luting products and storage conditions.

For SEM observation, specimens were fixed in Karnovsky's solution, post-fixed in osmium tetroxide and embedded in epoxy resin (Epoxycure, Buehler). Afterwards, they were polished with 400-, 600-, 1200-, and 2400-grit SiC paper and 6-, 3-, 1-, and 0.25-μm diamond paste (Arotec; Sao Paulo, SP, Brazil). Then, specimens were dehydrated in an ascending ethanol series and coated with carbon. Resin/dentin interfaces were observed with a scanning electron microscope (LEO 435 VP, LEO Electron Microscopy). Due to differences in hybrid layer thickness and in the magnification necessary to characterize the interfaces, no attempt was made to quantify the silver deposits. Representative images were chosen to depict the most frequently observed aspect of the resin/dentin interfaces in the different testing conditions.

RESULTS

Microtensile Bond Strength

Statistical analysis revealed significant differences for the resin cements ($p < 0.0001$) and for the water-exposure method ($p < 0.0001$) as well as the interaction between the two factors ($p < 0.0001$). The post-hoc test showed selective, significant differences in μTBS values among adhesives and water-exposure conditions ($p < 0.05$).

Mean μTBS values are presented in Table 2. At 24 h, the multi-step etch-and-rinse system RX presented the highest bond strength values, followed by the self-etching groups PS and PF, which were statistically similar. At 24 h, the self-adhesive cements presented significantly lower μTBS values than the multi-step systems, with no significant difference among them. However, GC, UC, and UN performed notably better than MC and SET. MC presented a high number of pre-test failures.

After 1 year of peripheral water exposure (1Yr-PE), the μTBS significantly decreased only for the etch-and-rinse system RX. However, RX still presented the highest μTBS values, which was not significantly different from PS and PF. Interestingly, 1Yr-PE specimens of GC and UN presented significantly higher values than 24h-PE groups. MC and SET presented the lowest values, with a high number of pre-test failures and were not significantly dif-

Table 2 Microtensile bond strength (MPa, mean ± SD) to dentin of the adhesive resins tested after the different storage conditions (n = 6)

Product type	Material [abbr.]	24-h peripheral water exposure (24h-PE) (pre-test failure/ number of beams)		1-year peripheral water exposure (1Yr-PE) (pre-test failure/ number of beams)		1-year direct water exposure (1Yr-DE) (pre-test failure/ number of beams)	
Two-step etch-and-rinse adhesive/resin cement	RelyX ARC + Single Bond [RX]	69.6 ± 16.6 (0/30)	Aa	51.5 ± 16.5 (0/30)	Ab	46.2 ± 4.3 (0/30)	Ab
Two-step self-etching adhesive/resin cement	Panavia F + SE Bond [PS]	49.2 ± 9.7 (8/30)	Ba	54.3 ± 7.1 (0/30)	Aa	44.8 ± 5.4 (0/30)	Aa
One-step self-etching adhesive/resin cement	Panavia F + ED Primer [PF]	33.7 ± 13.9 (0/30)	Ba	38.4 ± 8.9 (0/30)	ABa	13.6 ± 7.6 (10/30)	BCb
Self-adhesive cement	GCem [GC]	16.9 ± 10.3 (0/30)	Cb	32.5 ± 12.9 (0/30)	BCa	15.7 ± 15.3 (20/30)	BCb
Self-adhesive cement	RelyX U100 [UC]	15.3 ± 3.4 (0/30)	Ca	20.3 ± 8.5 (0/30)	CDa	10.8 ± 4.9 (4/30)	BCa
Self-adhesive cement	RelyX Unicem [UN]	12.5 ± 2.4 (3/30)	Cb	33.1 ± 10.4 (0/30)	BCa	25.5 ± 6.9 (0/30)	Ba
Self-adhesive cement	Maxcem [MC]	9.6 ± 7.7 (20/30)	Cab	14.3 ± 12.2 (13/30)	DEa	0.0 ± 0.0 (30/30)	Cb
Self-adhesive cement	Set [SET]	4.6 ± 0.5 (3/30)	Ca	2.7 ± 6.5 (28/30)	Ea	0.0 ± 0.0 (30/30)	Ca

Means followed by different letters (upper case – column, lower case – row) differ significantly, Tukey's test, at the 0.05 confidence level.

ferent from each other. GC and UN were not significantly different from PF after 1Yr-PE.

One year of direct water exposure (1Yr-DE) significantly reduced μTBS for RX, however, the μTBS values were not significantly different from those in the 1Yr-PE group. 1Yr-DE also reduced μTBS values for PF and MC. No beams could be tested for MC and SET at this storage period (100% pre-test failures). For GC, 1Yr-DE was not significantly different from the control group 24h-PE, but 1Yr-DE was significantly lower than 1Yr-PE. After 1Yr-DE, the highest μTBS values were observed for RX and PS, which were not significantly different from each other. After 1Yr-DE, GC, UN, and UC were not significantly different from PF. However, a high number of pre-test failures was observed for GC.

The distribution of failure modes among treatments is shown in Fig 1. The proportion of adhesive failures between cement and dentin increased after 1Yr-DE for RX, PF, UC, MC, and SET. For the self-adhesive cements, most of the failures were adhesive between cement and dentin, regardless of the storage condition (Figs 2A and 2B). The multi-step systems RX, PS, and PF presented a variety of failure modes, distributed across all failure patterns (Figs 2C and 2D). For PS, a decrease in the percentage of cohesive failures in the resin cement decreased after 1 year of storage in water, independent of the margins.

Nanoleakage

Representative SEM and TEM images of the nanoleakage patterns of the resin/dentin interfaces produced by the resin cements after the different storage conditions are presented in Figs 3 to 7. The characteristics of the resin/dentin interfaces produced by the multi-step systems and the silver deposition pattern were different between materials. The multi-step systems presented a distinct hybrid layer. The hybrid layer presented by the etch-and-rinse system RX was approximately 5 μm thick (Fig 3), whereas the hybrid layer produced by PF and PS was approximately 10 times thinner with 0.5 μm (Fig 4). RX presented the typical characteristics of etch-and-rinse systems: thick hybrid layer, funnel-shaped dentin tubules entrance, and long resin tags (Fig 3). Almost no silver deposition was observed for RX after 24h-PE, and increased silver deposition was observed after 1 year of storage in water (Fig 3). PF and PS presented the typical characteristics of mild self-etching systems: a thin, partially demineralized hybrid layer, measuring approximately 0.5 μm, and partially demineralized smear plugs, which result in small resin tags (Fig 4). Silver deposition was only detected under high magnification TEM. Tiny silver deposits were mainly observed at the top of the hybrid layer. The only difference between the interfaces presented by PF and PS was the approximately 6-μm-thick adhesive layer that

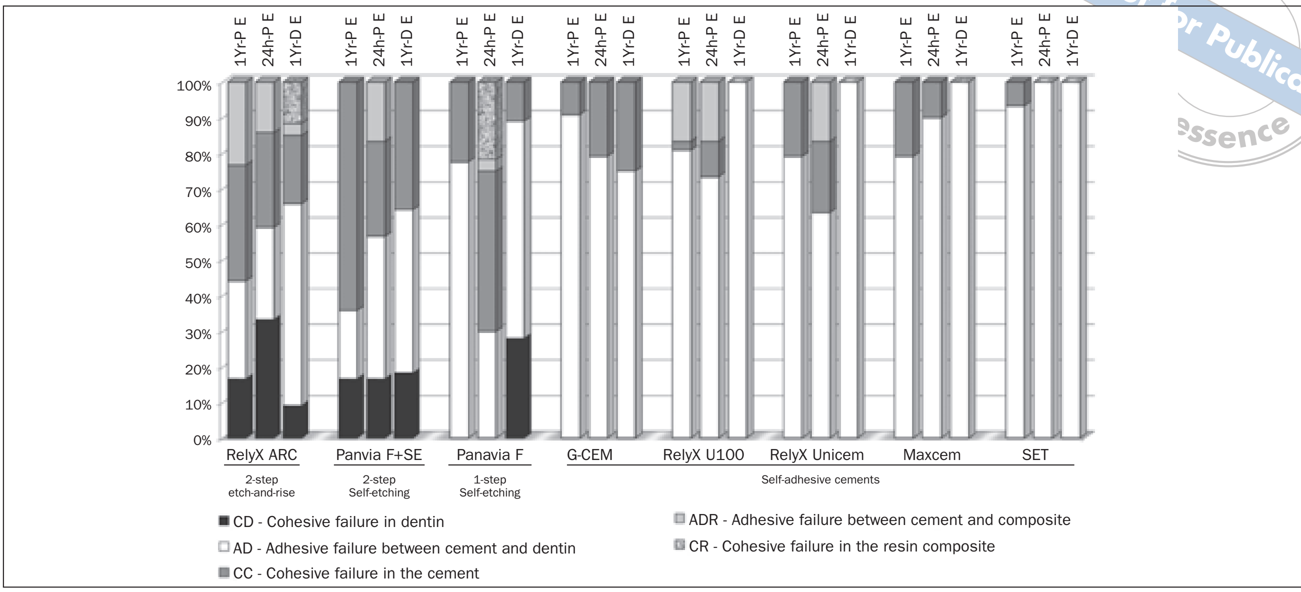

Fig 1 Distribution of failure modes among experimental groups: 24h-PE, 24 hours of peripheral water exposure; 1Yr-PE, one year of peripheral water exposure; 1Yr-DE, one year of direct water exposure.

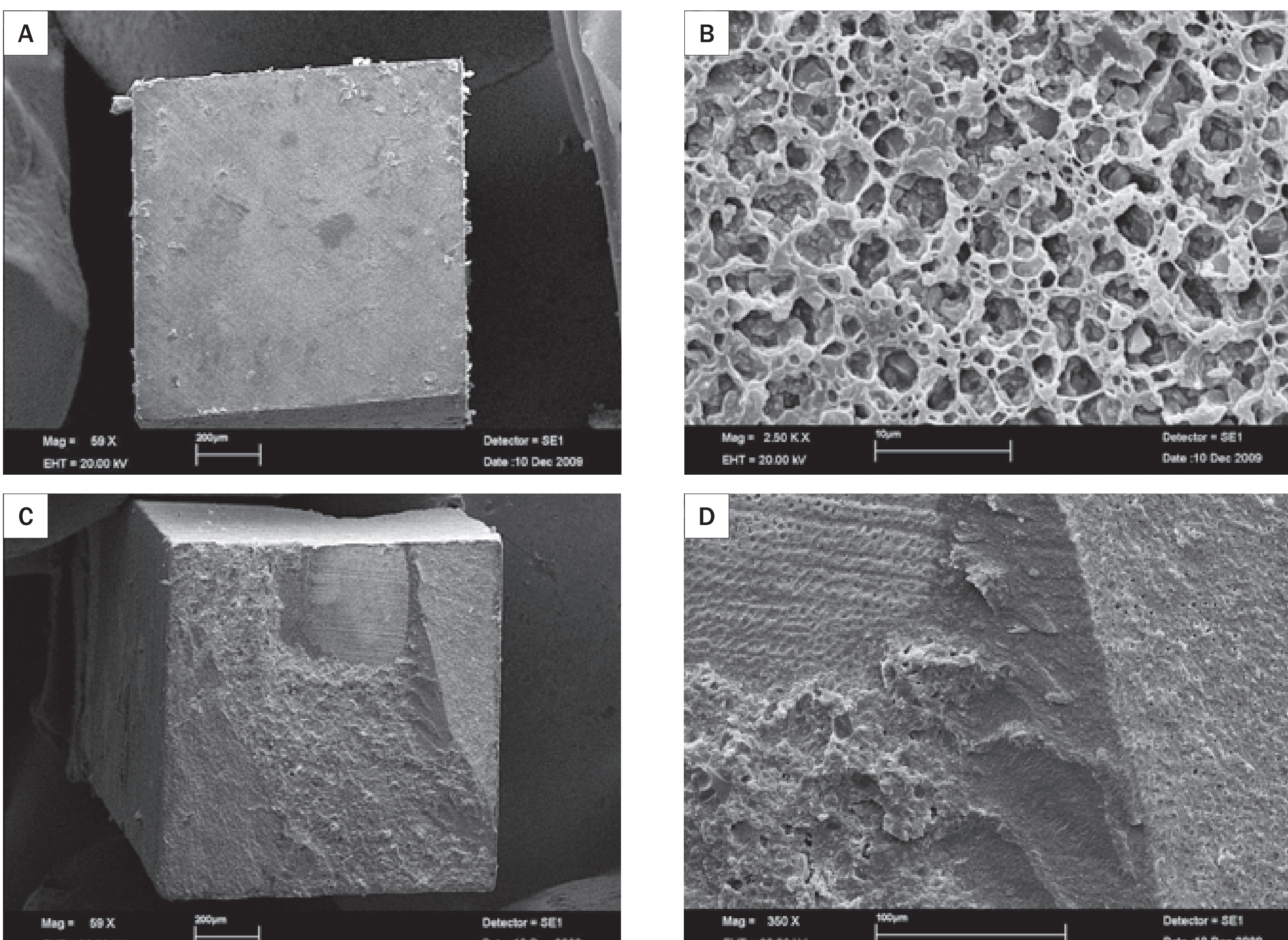

Fig 2 A and B: Representative SEMs of an adhesive failure of the self-adhesive resin cement GC after 1Yr-PE. 2A: Dentin side of fractured specimen. 2B: Higher magnification of the resin side of the same specimen. An irregular, porous surface was observed. 2C and 2D: Dentin side of a fractured specimen cemented with Panavia F and SE Bond after 1Yr-DE. The fracture occurred adhesively between the adhesive and dentin, and cohesively in the resin cement. 2C: Dentin side of fractured specimen; 2D: Higher magnification of 2C.

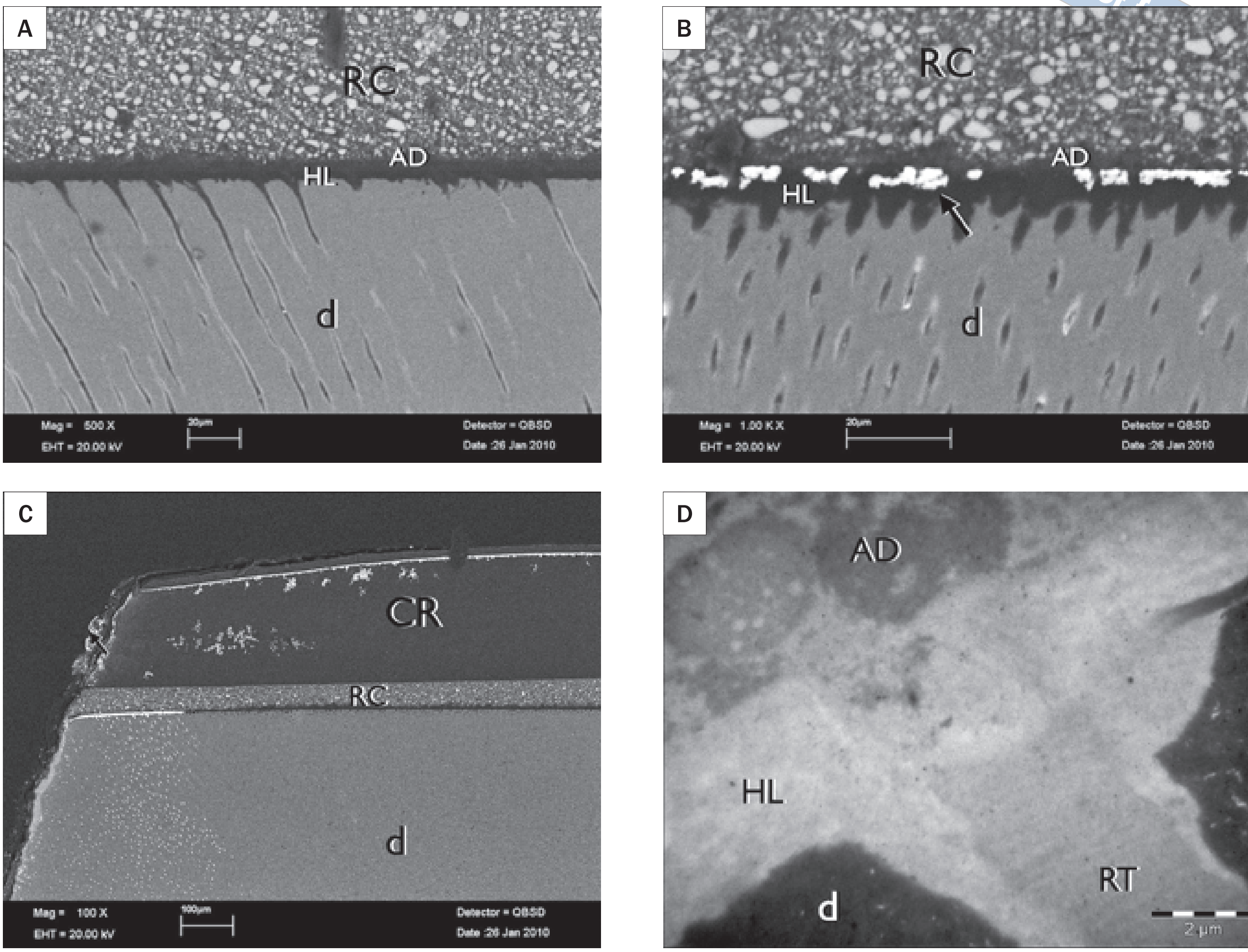

Fig 3 **Representative** images of the resin/dentin interfaces produced by the etch-and-rinse resin cement Rely X ARC. A, B, and C are backscattered SEMs of RX after 24h (A), 1Yr-DE (B) and 1Yr-PE (C). An increase in silver deposition was observed after 1 year, independent of the margin (arrow in B). D: TEM of the resin/dentin interface produced by RX after 24 hours. CR: composite resin, RC: resin cement, AD: adhesive, d: dentin, HL: hybrid layer, RT: resin tag.

was present due to the application of Clearfil SE Bond. Even though ED primer was applied over the polymerized adhesive system, it was not distinguishable under the TEM. An increase in silver deposition was only observed for PF after 1Yr-DE (Fig 4).

The resin/dentin interfaces produced by the self-adhesive cements presented characteristics and silver deposition patterns that were distinct from the multi-step systems and differed remarkably among the different self-adhesive materials. TEM observation revealed that UN had intimate contact with the dentin surface. It appears to incorporate the smear layer, slightly interacting with dentin. No silver deposition was observed for this system throughout the evaluation period (Figs 5A to 5D). On the other hand, UC, which is the clicker version of the same cement, presented some silver deposition at the interface at 24 h, but it was not observed after 1 year (Figs 5E to 5H). The self-adhesive cements UN and UC presented almost no silver deposition at the interfaces, regardless of the marginal substrate (Fig 5).

The self-adhesive cement GC appeared to infiltrate dentin deeper than the other self-adhesive resin cements. An interaction zone approximately 0.5 µm thick was observed. A basal zone of partially etched but uninfiltrated dentin was observed in some regions of this self-adhesive cement. Such a zone was characterized by the occurrence of silver deposits within the interfibrillar spaces of the mineralized dentin, and was located at a region beneath the hybridized complex (Fig 6). For the self-adhesive cement GC, the presence of an enamel margin was apparently beneficial for the integrity of the interface (Fig 6). For the self-adhesive cements MC and SET, one year of storage in water notably affected the integrity of the interfaces, because an increase of silver deposition and debonding of the resin cement were frequently observed (Fig 7).

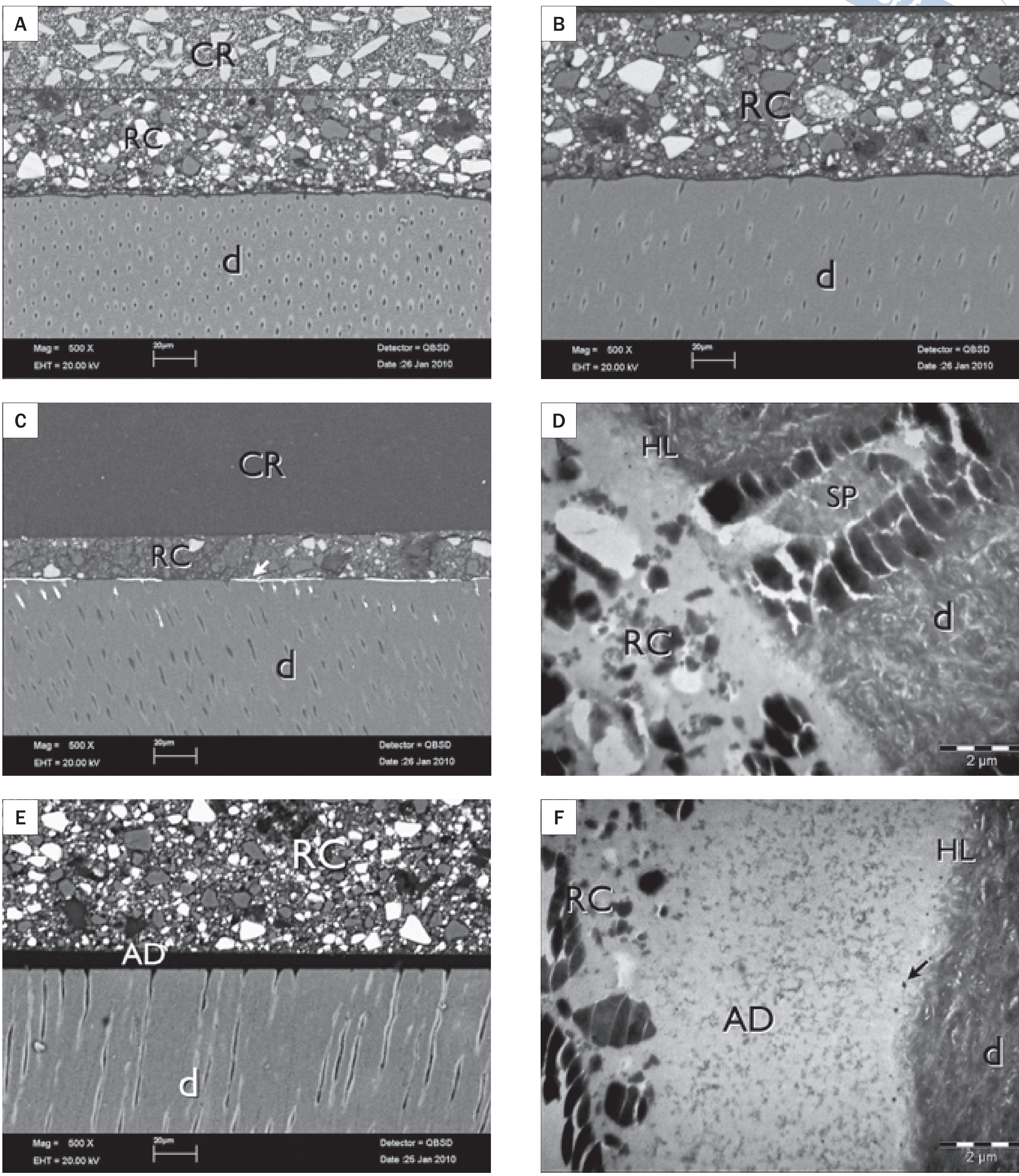

Fig 4 Representative images of the resin/dentin interfaces produced by the self-etching resin cement Panavia F. 4A, 4B, and 4C are backscattered SEMs of PF after 24h (A), 1Yr-PE (B) and 1Yr-DE (C). An increase in silver deposition was observed after 1Yr-DE (arrow, Fig 4C). 4D: TEM of the resin/dentin interface produced by PF after 24 hours. 4E and 4F: Representative images of Panavia F applied over the two-step self etching primer system Clearfil SE Bond (PS). 4E: resin/dentin interface produced by PS after 1Yr-DE. 4F: TEM of PS after 24 h. The arrow indicates tiny silver deposits on top of the hybrid layer. CR: composite resin, RC: resin cement, AD: adhesive layer; d: dentin, HL: hybrid layer, SP: smear plug.

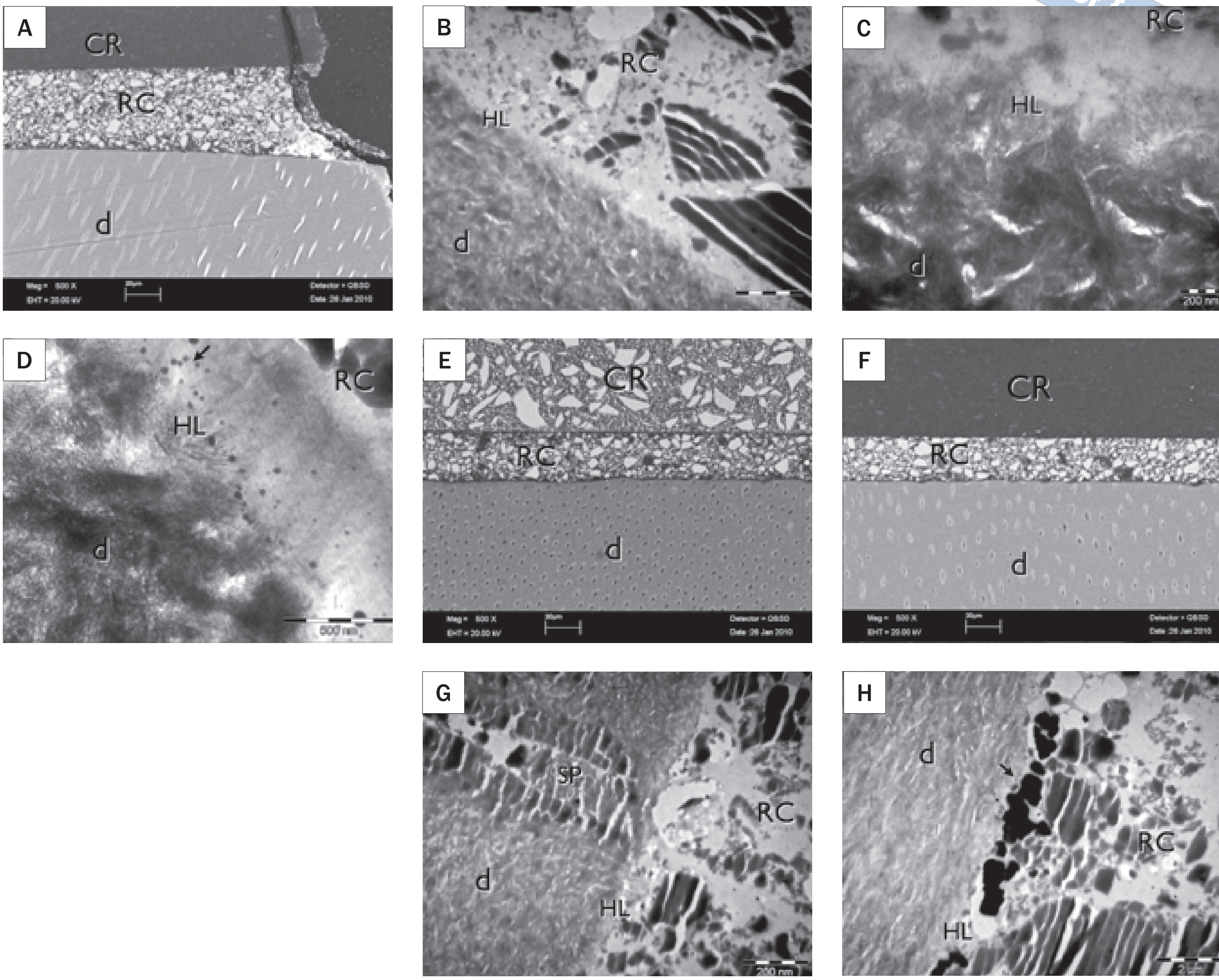

Fig 5 Resin/dentin interfaces produced by the self-adhesive cement RelyX Unicem. 5A: Backscattered SEM image of UN after 1Yr-DE. Very tiny silver deposits could be observed after 1Yr-DE. B, C, and D are TEM images of the resin/dentin interfaces produced by UN. 5B and 5C: 24 h; 5D: 1Yr-PE. The arrow in Fig 5D indicates tiny silver deposits on top of the hybrid layer after 1Yr-PE. 5E to 5H: resin/dentin interfaces produced by the self-adhesive cement RelyX U100. E and F are backscattered SEMs of UC after 24 h (E) and 1Yr-DE (F). G and H are TEM images of UC after 24 h. Some silver deposition was observed after 24 h (arrow). CR: composite resin, RC: resin cement, d: dentin, HL: hybrid layer, SP: smear plug. Resin/dentin interfaces produced by the self-adhesive cement RelyX Unicem. RC: resin cement, d: dentin, HL: hybrid layer, SP: smear plug.

DISCUSSION

In the present study, the bond strength of 5 self-adhesive cements was compared with conventional multi-step systems. An etch-and-rinse and a self-etching cement were used as control groups, and an additional group was used for comparison, in which a two-step self-etching primer adhesive system was used before the application of Panavia F. The first null hypothesis must be rejected, because significant differences in μTBS values and nanoleakage patterns were observed among the different luting materials. The greatest advantage of self-adhesive cements is the easy and fast application technique, which is one of the most desirable features in any dental material. Although the multi-step application technique has been reported to be complex and sensitive,[9] in the present investigation, the multi-step systems RX and PS presented higher bond strengths than self-adhesive cements in all storage conditions.

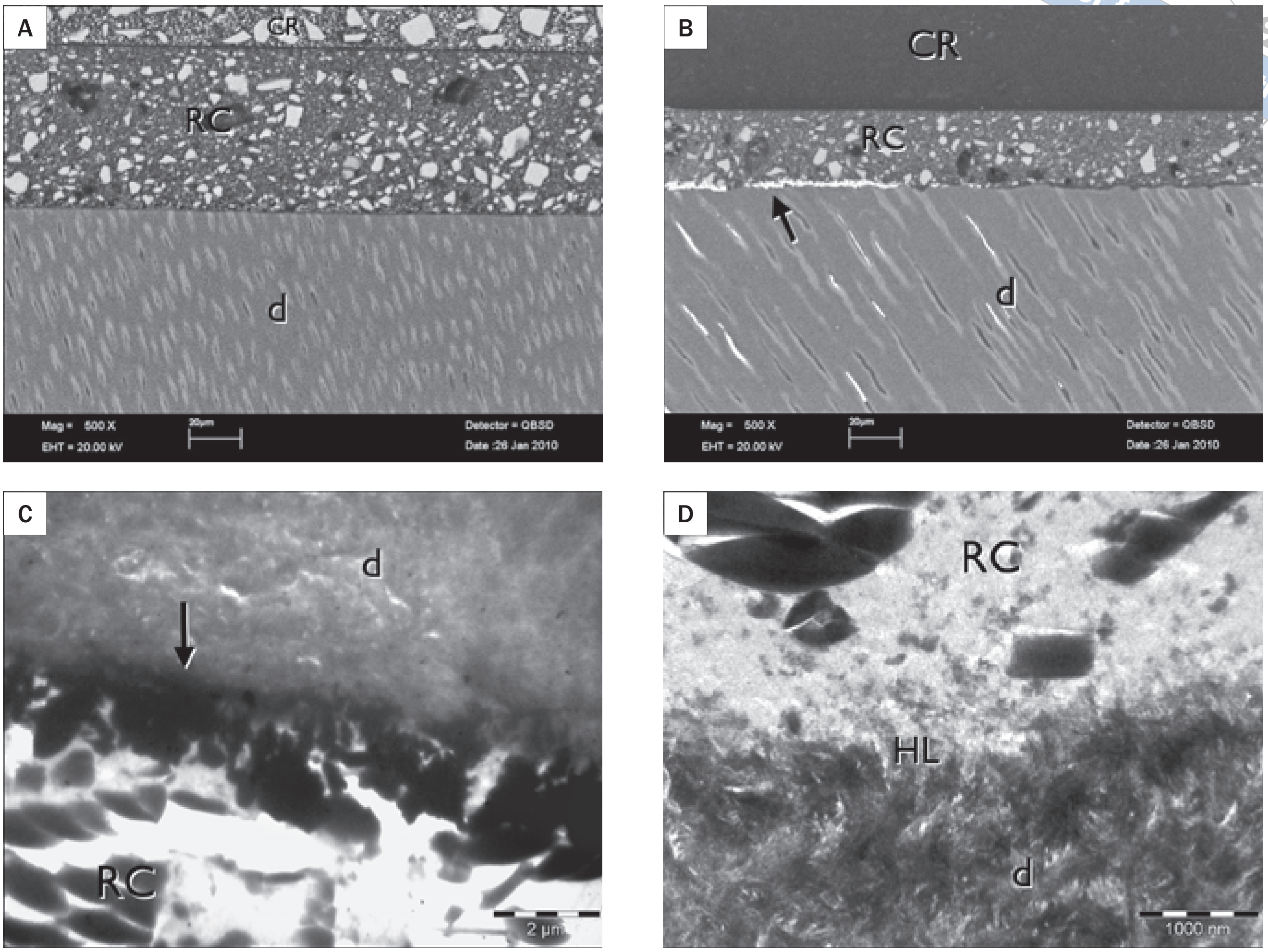

Fig 6 Resin/dentin interfaces produced by the self-adhesive cement G-Cem. A and B are backscattered SEM images of GC after 24 h (A), and 1Yr-PE (B). C: TEM of GC after 1Yr-DE. An increase in silver deposition was observed after 1Yr-DE (arrows in 6B and 6C). D: TEM image of GC after 24 h. CR: composite resin, RC: resin cement, d: dentin, HL: hybrid layer.

The second null hypothesis was also rejected, because a significant reduction was observed in µTBS strengths following long-term water immersion. A peripheral resin-enamel bond decreased the degradation rate in resin/dentin interfaces for most resin cements. Our results confirm other reports that hydrolytic degradation can affect resin/dentin interfaces.[19,20] However, the different resin cements tested presented distinctly different behaviors with respect to direct or peripheral water exposure during a 1-year evaluation period. The present study demonstrated that the presence of a composite-enamel bond adjacent to a composite-dentin bond might help protect the resin/dentin interface against degradation for most cements. Except for RX, stable µTBS values were observed for all resin cements after one year of peripheral water exposure (1Yr-PE).

After 24 h of storage in water, the self-adhesive systems presented µTBS values significantly lower than those produced by the multi-step systems RX, PS, and PF. PF specimens with margins in dentin and stored in water for 1 year showed a significant decrease in µTBS values, which were not significantly different from those exhibited by other self-adhesive cements. When the two-step self-etching adhesive Clearfil SE Bond was used prior to the application of the self-etching primer (ED primer), the bond strength was not altered, even after 1 year of direct water exposure. The hydrophobic adhesive layer probably reduced the permeability of the interface between dentin and resin cement. In addition, direct light activation of the adhesive system probably resulted in a better conversion of the monomers within the hybrid and adhesive layer.[15]

After 1 year of storage in water, GC, UN, and UC were not significantly different from PF. The self-adhesive cements U100 (UC) and Unicem (UN) were both developed by the same manufacturer and marketed under the same name in some countries. According to the manufacturer, the only difference between these products is the delivery system. While UN requires an activator, triturator and applicator, UC can be hand mixed due to its presenta-

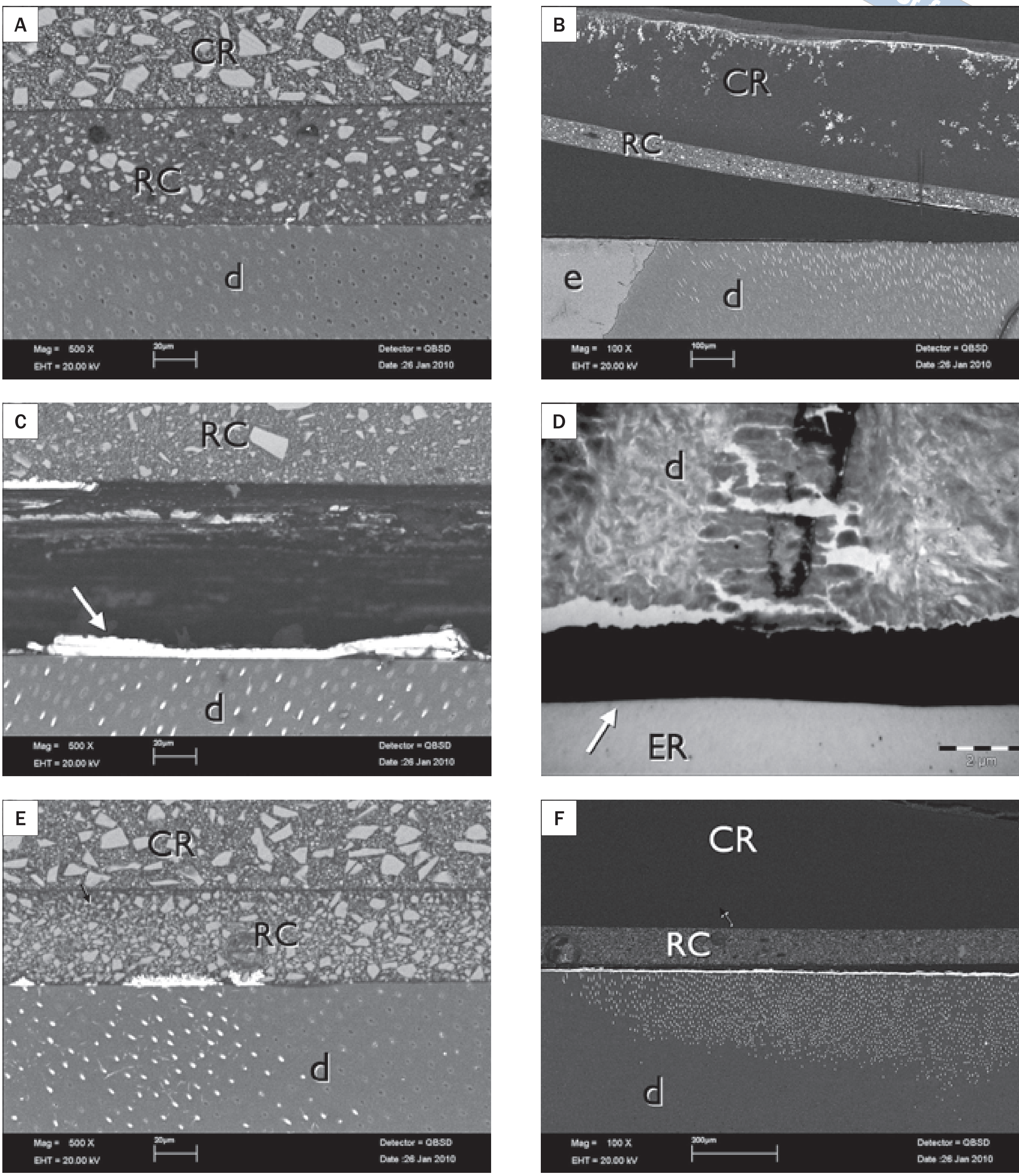

Fig 7 Resin/dentin interfaces produced by the self-adhesive cement Maxcem. A, B, and C are backscattered SEM images of MC after 24 h (A), 1Yr-PE (B) and 1Yr-DE (C). Gaps were frequently observed after 24 h and increased after 1 year. D: TEM of MC after 24 h. Arrows in C and D show large silver deposits. 7E and 7F: Resin/dentin interfaces produced by the self-adhesive cement SET after 24 h (E) and 1Yr-PE (F). Gaps and silver deposition were frequently observed after 24 h and increased after 1 year. CR: composite resin, RC: resin cement, d: dentin, e: enamel, ER: epoxy resin.

tion mode. Bond strength values were not significantly different between UC and UN. Interestingly, UN and GC μTBS values increased significantly after 1 year of storage in water. This finding suggests that the materials were not completely cured and had not achieved optimal mechanical properties after 24 h, when the first evaluation was performed. A similar behavior has been reported for some glass-ionomer and resin-modified glass-ionomer cements.[8] Interestingly, GC and UN possess some chemical components also present in glass ionomers.

Despite the low initial cement pH (< 2 in the first minute according to the manufacturer), almost no demineralization/infiltration was observed on the dentin surface for UN and UC (Fig 5). This finding is in agreement with the study performed by De Munck et al.[6] This might be attributed to the higher cement viscosity compared to self-etching primers, which hinders the resin cement in wetting and infiltrating the dentin surface.[6] A limited ability to demineralize and infiltrate dentin substrate has been reported for UN, which can explain why an extremely thin hybrid layer is formed when applied to dentin (Fig 5).[6,12,16] In order to promote micromechanical interlocking with dentin collagen fibrils, these cements should be able to etch the substrate in a relatively short time, requiring optimal wetting properties to ensure a fast interaction with dentin.[17] Chemical interaction with dentin hydroxyapatite has been reported for Unicem,[10] which may help explain the favorable bond strength results reported for this self-adhesive material.[18]

TEM observation of G-Cem revealed a deeper demineralization compared to UN and UC, of approximately 1 μm depth. However, high amounts of silver deposition were detected for GC (Fig 6). A basal zone of partially etched but uninfiltrated dentin was observed in some regions of this self-adhesive cement. Such a zone was characterized by the occurrence of silver deposits within the interfibrillar spaces of the mineralized dentin, and was located at a region beneath the hybridized complex. A similar pattern of silver deposition has been reported for some self-etching adhesives.[5] The bonding mechanism of GC has been reported by the manufacturer to be based on the glass-ionomer technology modified by exchanging polyacrylic acid with the acidic functional monomers 4-META and phosphoric-acid esters.[26] Water in the cement composition of GC is expected to aid the conditioning reaction, reducing the time needed for interacting with the substrate. However, the relatively weak chemical bonding potential of 4-META and the high molecular weight of the functional monomer are expected to make only a small contribution to the supposed chemical reaction within a clinically reasonable time.[25]

The lowest bond strengths were observed when the self-adhesive cements MC and SET were used. After 1 Yr-DE, no specimens could be tested for these systems, because specimens debonded prematurely during storage. Massive silver deposition and gaps were observed for these systems (Fig 7). According to the manufacturers, the self-etching capacity is attributed to the presence of different monomers in the luting agent formulation, such as GPDM in Maxcem and methacrylated phosphoric esters in SET. Han et al[13] reported low pH values for GC, MC, and UN a few seconds after manipulation. However, after 48 h, only UN presented a neutral pH (pH 7.0). According to those authors, the pH reported 48 h after polymerization was 2.4 for MC and 3.6 for GC. Even though an initially low pH is important for etching of enamel and dentin, if a low pH is maintained for a longer period, it can adversely influence the adhesion of the mixed cement to dentin.[13,24]

CONCLUSION

In summary, all self-adhesive luting agents evaluated in the current study yielded lower bond strength values than the multi-step systems RX and PS. The presence of enamel margins was effective in reducing the degradation rate for PF, GC, and MC. Among the self-adhesive cements, UN and UC presented the lowest silver deposition and most stable bond strengths over the course of the experiment. GC presented high amounts of silver deposits, and MC and SET with dentin margins did not resist specimen preparation procedures after 1 year of water storage. Among the tested self-adhesive cements, UN and UC seem to be more indicated for luting indirect materials to tooth substrate.

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Clinical relevance: Clinicians should be aware that multi-step resin cements promote higher short- and long-term bond strength to dentin than self-adhesive cements, but should also expect better long-term performance of indirect restorations for both types of resin cements when enamel margins are present.