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Fluoride Ion Release of Self-Adhesive Resin Cements and Their Potential to Inhibit *In Situ* Enamel and Dentin Demineralization

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Clinical Relevance

Fluoride release and demineralization inhibition in enamel and dentin of self-adhesive resin cements varied within brands and was mostly lower than that of conventional glass ionomer cement.

SUMMARY

Objective: This study evaluated *in situ* the potential of a glass ionomer and self-adhesive resin cements to inhibit enamel and dentin demineralization around indirect restorations exposed to cariogenic challenge. The cumulative fluoride release (CFR) of materials was measured in water and acid. Methods: Seventy blocks cut from human molars received two indirect composite restorations (one in enamel and another in dentin) luted with Ketac Cem EasyMix (GIC, positive control), SeT (SeT), Maxcem Elite (Max), Smart Cem2 (Smart), and RelyX Unicem 2 (Unicem2). Fourteen volunteers wore palatal appliances containing five blocks exposed to a cariogenic challenge (20% sucrose solution, eight times per day, seven days). Knoop microhardness (KH) at two distances from the margins and three depths from the outer surface determined enamel and dentin demineralization. Disc-shape specimens of materials were immersed in daily-replaced deionized water or lactic acid solutions. KH and CFR data were analyzed by analysis of variance, Games-Howell test, and Tukey test (α=0.05). Results: The overall KH ranking was GIC > SeT > Max > Smart = Unicem2 in both enamel and dentin (">" means *p*<0.05). SeT was the only resin cement that resulted in enamel and dentin KH comparable

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to that of GIC at most distances and depths. In water, CFR rank of materials was GIC > SeT = Max > Smart = Unicem2. In acid, the rank was similar, except that Set was significantly superior to Max. Conclusion: SeT inhibited demineralization in enamel and dentin quite comparably to GIC. All resin cements released lower cumulative amounts of fluoride than the glass ionomer cement.

INTRODUCTION

Secondary caries make up the most important cause of failure and replacement of direct[1] and indirect dental restorations.[2] Fluoride-releasing materials supposedly help prevent or reduce caries progression, which could decrease the need for additional restorative treatments. Glass ionomer cement (GIC), resin-modified glass ionomer cement, polyacid-modified composite (compomer), composite, and adhesive systems are fluoride-containing dental restoratives available on the market.[3]

The cariostatic properties of restorative materials are associated with the amount of fluoride released and incorporated into the adjacent tooth structure.[4] Fluoride is intentionally added to materials as an anticaries component, or the fluoride is released as part of the natural setting reaction of the material (eg, glass ionomers).[5] Fluoride release varies according to the source, size, and concentration of fluoride-containing filler particles as well as the composition, solubility, and permeability of the resin matrix in composite materials.[5-8]

Luting procedures of indirect restorations include the use of zinc phosphate, glass ionomer, and resin cements. Fluoride-containing luting cements could be effective in preventing or reducing secondary caries around the edges of indirect restorations. Glass ionomer and zinc phosphate luting cements have been investigated regarding their effect against secondary caries in enamel and root dentin adjacent to indirect restorations.[9,10] Self-adhesive resin cements (SARCs) were developed with claims of shorter application time and less technique sensitivity. SARCs act through a mechanism of infiltration on dental tissues combined with a chemical reaction between phosphate methacrylates and hydroxyapatite crystals.[11,12] Although some SARCs contain fluoride sources in their composition, limited information exists regarding their fluoride release,[13] and no data are available regarding their potential to reduce or prevent demineralization on the enamel and root dentin adjacent to indirect restorations exposed to a cariogenic challenge.

The anticaries mechanism of restoratives containing fluoride was previously evaluated by *in situ* studies.[14-17] This model reproduces the dynamics of caries development on either enamel or dentin using palatal appliances by promoting demineralization of the tooth surface. Different treatment strategies for the prevention or control of carious lesions are tested in a controlled manner and during a short period of time.[18,19] Moreover, the model provides a link between clinical and laboratory conditions.[18]

The objectives of this study were 1) to evaluate the *in situ* effect of fluoride-containing self-adhesive resin cements on the decrease of enamel and root dentin demineralization under cariogenic challenge and 2) to evaluate the cumulative release of fluoride ions from the cements in water and in an acidic solution. The two null hypotheses tested were that there would be no difference among hardness of enamel and root dentin adjacent to the cements and no difference among the cumulative fluoride release of the cements.

METHODS AND MATERIALS

Experimental Design

The factors under study for anticaries effect were luting cement at five levels—one conventional glass ionomer and four self-adhesive resin cements—and position at six levels—each one uniquely determined by one of the two distances from the preparation margin and one of the three depths from the outer enamel and dentin surface.[20] The factors under study for cumulative fluoride release were the luting cement and media solution at two levels: deionized water and lactic acid.

Anticaries Effect

A randomized, double-blind *in situ* design was conducted in one phase of seven days, during which 14 volunteers wore palatal appliances containing five human dental blocks containing indirect restorations luted with five cements in enamel and dentin cavities. Thirty-five sound third human molars that had been extracted and stored in the Pontifícia Universidade Católica do Paraná Tooth Bank were used. The inclusion criteria were sufficient volume of root and absence of caries lesions and fractures or imperfections in enamel and root dentin. Dental surfaces were manually scaled and then cleaned using a rotary bristle brush with a slurry of pumice and water. The cleaned teeth were stored in 0.05% chloramine-T solution at 4°C for a maximum of four months. The cervical third of each crown and root

Table 1: *Materials Used in the Present Study*

Group	Material (Manufacturer)	Composition[a] (Lot Number)
Unicem 2	RelyX Unicem2 (3M ESPE, St Paul, MN, USA)	Base paste: methacrylate monomers containing phosphoric acid groups, silanated glass powder, initiator components, stabilizers, rheological additives. Catalyst paste: methacrylate monomers, alkaline (basic) fillers, silanated fillers, initiator components, stabilizers, pigments, rheological additives. (1312800922)
Smart	Smart Cem2 (Dentsply, Weybridge, UK)	Base paste: silanated barium-boron-fluoro-alumino-silicate glass, polymerizable dimethacrylate resin, strontium fluoride, hydrophobic amorphous silica. Catalyst paste: barium boron fluoro-alumino-silicate glass, urethane dimethacrylate resin, urethane modified bisphenol-A-diglycidylether dimethacrylate (Bis-GMA), dipentaerythritol pentaacrylate phosphate, hydrophobic amorphous silica. (120419)
Max	Maxcem Elite (Kerr, Orange, CA, USA)	Glycerol dimethacrylate dihydrogen phosphate, multifunctional methacrylate monomers, proprietary self-curing redox activator, camphorquinone, stabilizer. Filler load (67%wt): fluoro-aluminio-silicate glass, fumed silica, barium glass, ytterbium fluoride. (506742)
SeT	SeT PP (SDI, Bayswater, Australia)	Fluoro-alumino-silicate glass (60 to 70%wt), urethane dimethacrylate, camphorquinone, acidic monomer. (S1303061)
GIC	Ketac Cem EasyMix (3M ESPE)	Powder: aluminum-calcium-lanthanum-fluorosilicate glass. Liquid: water, copolymer of acrylic maleic, tartaric and benzoic acid. (524470)

[a] *Data provided by the manufacturer.*

was sectioned longitudinally and transversally into 70 blocks using a diamond disc (D943-100, Kerr Rotary, Orange, CA, USA). Each block had the side opposite to the restoration manually ground to achieve a 2-mm thickness using #1200 SiC sandpaper. The final dimensions (7×4 mm) of the blocks were checked with a digital caliper (CD-15CX, Mitutoyo Corp, Tokyo, Japan). Two cavities (1.5-mm depth×1.5-mm diameter)—one in enamel and the other in dentin—were prepared on each block using a cylindrical diamond self-limiting bur (MADC-015, Kerr Rotary) under constant water cooling. The diamond burs were replaced every 10 preparations (five blocks). The blocks were stored at 37°C and at 100% relative humidity for 24 hours.

The dental blocks were sterilized by autoclaving and randomly divided into five experimental groups (n=14). The cavities received indirect restorations of a resin-based laboratory composite (SR Adoro, Ivoclar Vivadent, Schaan, Liechtenstein). Luting materials consisted of four translucent dual-cured self-adhesive resin cements and one conventional glass ionomer cement (positive control). The materials were manipulated according to the manufacturers' instructions. Details of the materials are presented in Table 1. The resin cements were light cured for 40 seconds with a light-curing device (Elipar Free Light II, 3M ESPE, St Paul, MN, USA) monitored to 1000-mW/cm^2 irradiance every five specimens.

Fourteen adult subjects (six males and eight females; mean age 21 years, range 18 to 25 years) were selected for the *in situ* study. The inclusion criteria were 1) good general and oral health, 2) low caries activity, 3) nonusage of antibiotics two months prior to the study, 4) nonsmoker, and 5) no history of ingestion of drugs that affect salivary flow. The exclusion criteria were 1) any infectious disease, 2) not having used the sucrose solution in accordance with the research recommendations, and 3) poor oral hygiene. All volunteers signed the informed consent form detailing the main aspects of the research and all recommendations and guidelines regarding the procedures performed during the experiment.

Acrylic palatal appliances were constructed for each volunteer with five cavities (8×5×3 mm) for the restored blocks. A polyester mesh was positioned over the blocks to protect their surfaces from mechanical attrition, leaving a 1-mm space for biofilm accumulation.

The volunteers used the appliance for seven days. A previous study[21] showed that 20% sucrose exposure (eight times per day) significantly induced mineral loss of enamel after seven days of biofilm accumulation. Oral hygiene was performed three times a day with a fluoride toothpaste (Colgate Toothpaste Triple Action, 1500 mg F/g, Colgate-Palmolive Company, North York, ON, Canada) and a soft bristle dental brush (Oral-B Advantage Plus Soft Bristle Toothbrush, Procter & Gamble, Cincinnati, OH, USA) given by the main researcher. The appliances were not brushed to avoid disturbing the biofilm. The volunteers were advised to remove the appliance only during meals and oral hygiene. The cariogenic challenge was carried out by drop-

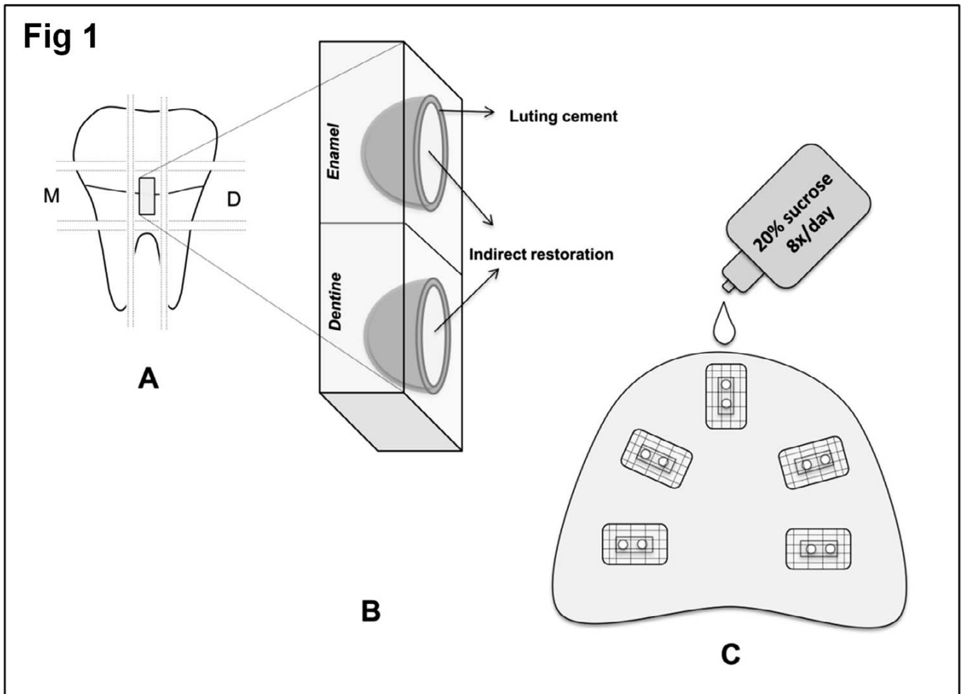

Figure 1. *(A): Schematic illustration of tooth (M, mesial; D, distal) sectioning to obtain blocks. (B): The location of indirect restorations in enamel and dentin. (C): The palatal appliance challenged with 20% sucrose solution.*

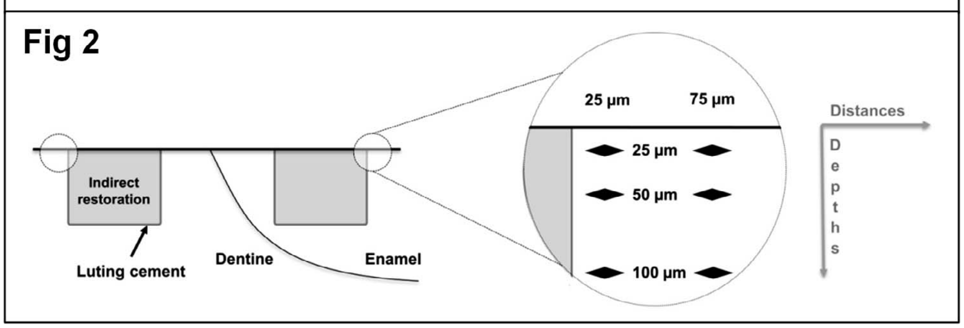

Figure 2. *Schematic representation of indirect restorations and the location of Knoop hardness indentations at two distances (25 and 75 μm) from the preparation margins and three depths (25, 50, and 100 μm) from the outer surface in enamel and dentin.*

ping a 20% sucrose solution eight times per day on each block at predetermined times. After five minutes, the appliance was reinserted in the mouth (Figure 1).[15,22,23]

Following the *in situ* phase, the blocks were laterally included in an epoxy resin and manually polished to expose the inner part of the blocks for Knoop microhardness testing. Polishing was performed under water cooling with #1200 and #2000 SiC sandpaper followed by polishing with a 0.25-micron and a 1-micron diamond paste. The blocks were cleaned with deionized water in an ultrasonic bath for 10 minutes before each sandpaper and paste and after the last polishing.

The Knoop microhardness of the enamel and dentin was measured with a microhardness tester (HMV-2T, Shimadzu Corp, Tokyo, Japan) set at 10*g* for 15 seconds for dentin and 25*g* for 15 seconds for enamel. Indentations were made at 25- and 75-μm distances from the preparation margin and at 25-, 50-, and 100-μm depths from the outer enamel and dentin surface (Figure 2).[20]

Analysis of Fluoride Release

The materials were inserted into Teflon matrices (11 mm in diameter and 1.5 mm in thickness) and pressed between two Mylar strips and glass slides on top and bottom surfaces. The resin cements were light cured on both surfaces for 40 seconds with a light-curing device (Elipar Free Light II, 3M ESPE) and monitored to 1000-mW/cm^2 irradiance every five specimens. Glass ionomer cement was placed on the matrix, pressed for one minute with two glass slides, and allowed to cure for seven minutes. The specimens were removed from the matrices, and excess material was carefully removed by using a surgical blade. After setting time, the GIC specimens were protected with a protective varnish. The materials were inserted in the matrix together with a cotton rope that later kept the specimens suspended inside the tubes.

Table 2: *Mean Values of Knoop Microhardness of Enamel at Different Distances (DI) and Depths (DE)[a]*

DI	DE	GIC	SeT	Max	Smart	Unicem2
25	25	215.37 (7.86) ABCa	203.14 (15.74) ABab	191.57 (7.88) ABCb	158.50 (9.56) Ac	155.19 (14.61) Ac
25	50	221.50 (7.61) ABa	208.00 (7.59) Aab	198.93 (8.03) ABb	162.57 (9.33) Ac	161.27 (14.98) Ac
25	100	222.02 (7.70) Aa	205.21 (11.32) Ab	202.00 (6.40) Ab	169.43 (9.04) Ac	166.55 (14.43) Ac
75	25	200.69 (7.95) Ca	189.50 (12.94) Bab	178.50 (6.31) Cb	157.93 (9.95) Ac	155.44 (12.99) Ac
75	50	206.96 (7.81) BCa	194.36 (13.56) ABab	180.71 (7.09) Cb	160.07 (9.53) Ac	159.74 (12.54) Ac
75	100	208.01 (6.68) ABCa	195.14 (13.28) ABab	185.79 (6.35) BCb	165.07 (8.54) Ac	163.05 (13.44) Ac

[a] *Standard deviations are in parentheses. Mean values with different letters differ statistically ($p<0.05$) in columns (uppercase), comparing distances and depths in the same material, and rows (lowercase), comparing the different materials in the same distances and depths.*

All samples were kept in an oven at 37°C for 24 hours under relative humidity conditions. The GIC discs were then finished and polished (Sof-Lex Finishing and Polishing System, 3M ESPE) under water cooling to remove the varnish layer.[24]

Six specimens from each material were individually immersed in 3 mL of deionized water (ISO FDIS 4049:1999), while six other such specimens were individually immersed in 3 mL of 5 nM lactic acid (pH 5), which accounts for 70% of the total acid found in human dental plaque.[25,26] Specimens were incubated in plastic tubes for 15 days under constant stirring at a temperature of 23°C ± 1°C. The immersing solutions were replaced daily, and the discs were washed in deionized water and dried with paper before changing tubes. The solutions from days 1, 2, 3, 4, 7, 9, 11, 14, and 15 were stored at 4°C in sealed plastic tubes, and those from days 5, 6, 8, 10, 12, and 13 were discarded.

The fluoride concentration of the stored solutions was analyzed in triplicate by adding equal volume of total ionic strength adjustment buffer (TISAB II) solution (1.0 M acetate buffer, pH 5.0, containing 1.0 M NaCl and 0.4% 2-[(2-[bis(carboxymethyl)amino]cyclohexyl)-(carboxymethyl)amino] acetic acid [CDTA]). The analysis was performed using a specific fluoride electrode (ThermoOrion 96-09, Thermo Scientific Fisher, Carlsbad, CA, USA) coupled to an ion analyzer (ThermOrionStar A211, Thermo Scientific Fisher) and calibrated with standard fluoride solutions (0.016 to 32.0 μg F^-/mL in 50% TISAB II). The fluoride concentrations in the media were measured, and the amount of fluoride release was calculated as a function of area (μg F/cm^2).

Statistical Analysis

Normality and homogeneity of variance of Knoop microhardness data were checked with the Shapiro-Wilk and Levene tests. Data were then analyzed by two-way analysis of variance (ANOVA) (factors: material and position). Multiple comparisons were performed by the Games-Howell test (material) and the Tukey test (position). All tests were performed with the SPSS version 22 statistical package ($\alpha=0.05$).

Two-way ANOVA and the Games-Howell test were used for the statistical analysis of fluoride release ($\alpha=0.05$).

The mean cumulative fluoride release (μg F/cm^2) within the first seven days for each cement and the corresponding mean microhardness were compared by the Spearman correlation test ($\alpha=0.05$).

RESULTS

Enamel and Dentin Microhardness

The mean Knoop microhardness values of enamel and dentin at the different distances and depths from the indirect restoration margins are shown in Tables 2 and 3.

Table 3: *Mean Values of Knoop Microhardness of Root Dentin at Different Distances (DI) and Depths (DE)[a]*

DI	DE	GIC	SeT	Max	Smart	Unicem2
25	25	56.98 (5.23) ABCa	47.64 (5.69) Ab	42.36 (4.97) Bbc	37.57 (3.86) Bc	35.61 (8.38) Bc
25	50	58.28 (5.09) ABa	52.57 (4.65) Aab	48.57 (5.60) ABbc	42.93 (3.10) ABc	43.05 (7.07) ABc
25	100	61.16 (6.75) Aa	55.21 (5.25) Aab	51.14 (4.26) Ab	47.43 (5.26) Ab	47.53 (6.46) Ab
75	25	49.00 (5.08) Ca	48.71 (6.22) Aa	44.50 (6.36) ABab	37.50 (4.69) Bb	36.51 (10.78) Bb
75	50	50.92 (6.00) BCa	48.79 (5.22) Aa	44.36 (4.58) ABab	38.50 (4.24) Bb	37.81 (6.77) Bb
75	100	53.40 (5.12) ABCa	53.43 (5.26) Aa	48.57 (5.96) ABab	42.00 (4.95) ABbc	40.12 (7.93) ABc

[a] *Standard deviations are in parentheses. Mean values with different letters differ statistically ($p<0.05$) in columns (uppercase), comparing distances and depths in the same material, and rows (lowercase), comparing the different materials in the same distances and depths.*

Table 4: *Cumulative Fluoride Release (µg F/cm[2]) of Luting Cements Immersed in Acid or Water During the First Seven Days and Their Percentage Increase (%) in Release from Water to Acid[a]*

Material	Water	Acid	Water/Acid Ratio
GIC	6.0 (4.5) Aa	19.3 (7.1) Ab	0.310
SeT	1.5 (0.6) Ba	10.7 (4.2) Bb	0.140
Max	1.2 (0.7) Ba	6.0 (3.3) Cb	0.200
Smart	0.5 (0.2) Ca	3.9 (2.6) Db	0.128
Unicem2	0.1 (0.1) Da	2.1 (2.3) Eb	0.047

[a] *Standard deviations are in parentheses. Mean values with different letters differ statistically (p<0.05) in columns (uppercase), when comparing the materials, and rows (lowercase), when comparing the solution of immersion.*

In enamel hardness, GIC was statistically superior ($p<0.05$) to SeT at 25-µm distance and 100-µm depth and to Max at all distances and depths. Both Smart and Unicem2 showed the lowest hardness means for enamel at all sites when compared to the other groups ($p<0.05$). The 25- and 75-µm distances differed at 50-µm depth in GIC and Max and at 100-µm depth in Max ($p<0.05$). No other comparison was statistically significant.

In root dentin hardness, GIC was statistically superior ($p<0.05$) to SeT (at 25-µm distance and 25-µm depth), to Max (all depths at 25-µm distance), and to Smart and Unicem2 in all sites ($p<0.05$). SeT was superior to Smart at 25-µm distance and 25-µm depth and 75-µm distance in all depths and to Unicem2 at all sites except at 25-µm distance and 100-µm depth ($p<0.05$). Max differed from Smart and Unicem2 only at 75-µm distance and 100-µm depth ($p<0.05$). At 25-µm distance, the hardness at 100-µm depth was statistically higher than that at 25-µm depth in Max, Smart, and Unicem2. No other comparison was statistically significant.

Fluoride Release

Table 4 presents the mean cumulative fluoride release (µg F/cm^2) in acid and water during the first seven days for each luting cement. The fluoride release was statistically higher in acid than in water ($p<0.05$).

When immersed in water, the GIC showed the highest cumulative fluoride release among the tested materials ($p<0.05$). SeT and Max demonstrated similar amounts of cumulative fluoride release ($p>0.05$) but statistically lower than GIC ($p<0.05$). The lowest rates were observed in Smart and Unicem2, which differed statistically from each other as well as from the other materials ($p<0.05$).When immersed in acid, the cumulative fluoride release of all materials differed from each other ($p<0.05$), with the highest average observed for GIC.

Table 5: *Equations and R^2 Values for the Factor Time, Within Each Level of the Factor Material*

Media	Water		Acid	
Material	Equation	R^2 (%)	Equation	R^2 (%)
GIC	$Y = 11.721\ X^{-0.852}$	92.8	$Y = 28.670\ X^{-0.419}$	93.0
SeT	$Y = 2.381\ X^{-0.562}$	89.9	$Y = 19.039\ X^{-0.644}$	95.2
Max	$Y = 1.871\ X^{-0.510}$	72.4	$Y = 12.205\ X^{-0.833}$	96.1
Smart	$Y = 0.735\ X^{-0.500}$	81.0	$Y = 8.634\ X^{-0.995}$	96.8
Unicem2	$Y = 0.177\ X^{-0.611}$	78.9	$Y = 5.916\ X^{-1.596}$	97.1

The fluoride release of the tested materials was measured on a daily basis, and all of them were observed to follow the same pattern of fluoride release. The highest amounts were detected during the first days, tending to decrease with time (Figures 3 and 4).

The fluoride release curves were adjusted to estimate the mean values of fluoride release over 15 days by using the exponential function $Y = \alpha X^{\beta}$ (Table 5), where Y is the mean cumulative fluoride release at a given time, α and β are constants for each material, and X is the variable "time" in days.

The mean cumulative fluoride release in water and lactic acid during the first seven days for each luting cement correlated positively with the overall mean hardness value of enamel (water: $R=0.82$, $p=0.08$; acid: $R=0.92$, $p=0.02$) and dentin (water: $R=0.86$, $p=0.06$; acid: $R=0.95$, $p=0.01$). In addition, statistically significant and positive correlations were detected between enamel and dentin hardness means ($R=0.99$, $p=0.001$) and between cumulative fluoride release means in water and acid ($R=0.96$, $p=0.008$).

DISCUSSION

The null hypotheses were rejected, as the potential to release fluoride and to inhibit demineralization in enamel and root dentin varied between the luting cements. The tooth/restoration interface affects the uptake of fluoride from restorative materials by increasing its concentration and creating a greater on-site diffusion potential.[3] In the present study, the interface between the indirect restoration and the tooth structure allowed the cement film to release fluoride, which could act through the liquid phase adjacent to the tooth structure, preventing its demineralization.[27]

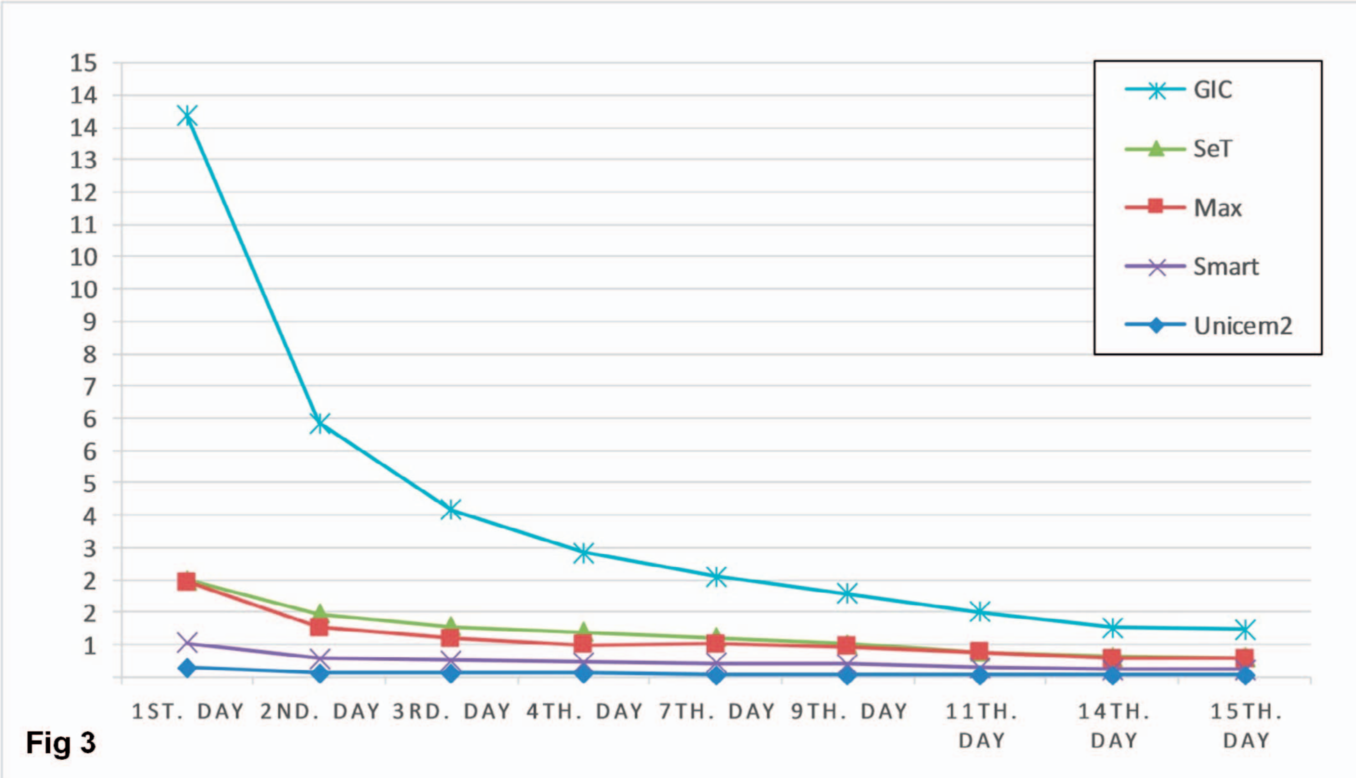

Figure 3. *Daily fluoride release mean (µg F/cm^2) in water.*

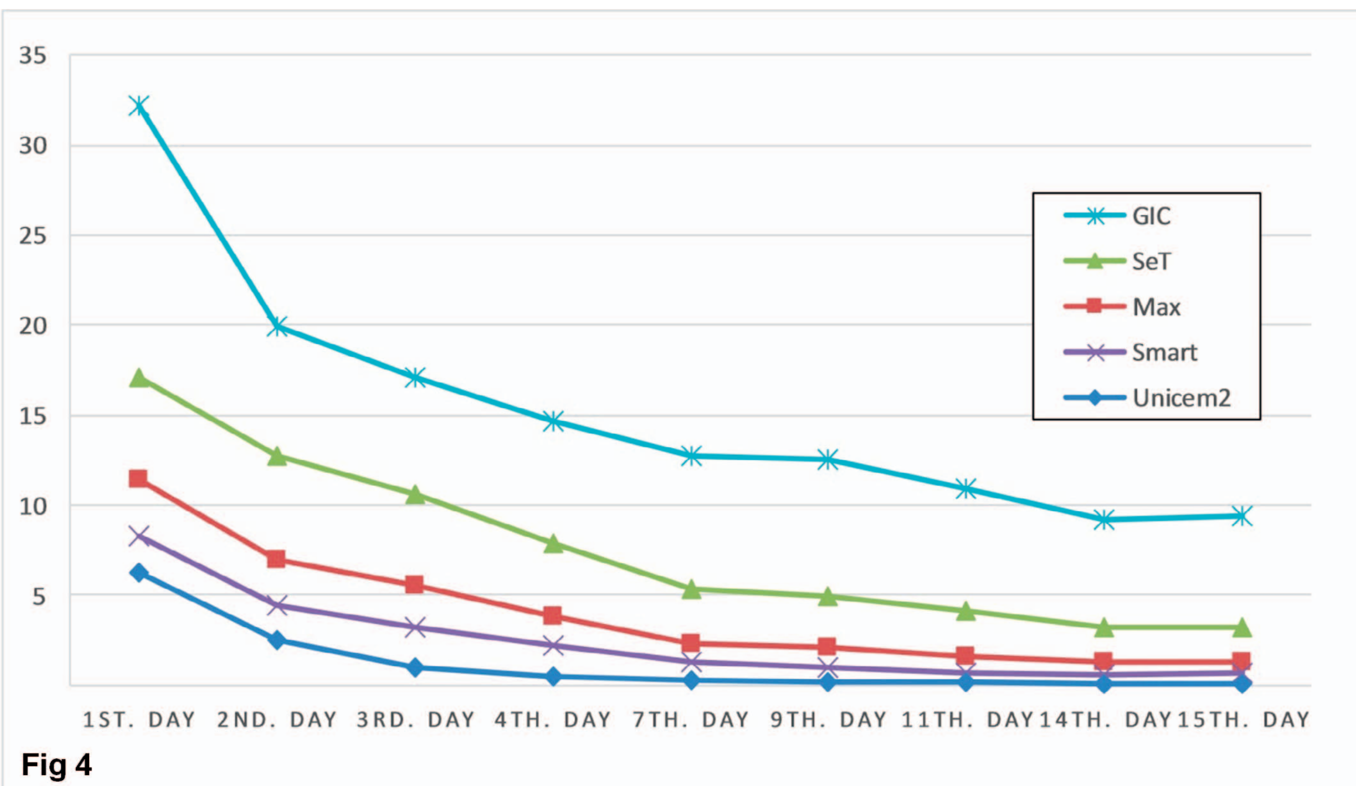

Figure 4. *Daily fluoride release mean (µg F/cm^2) in lactic acid.*

Knoop microhardness was evaluated at two distances from the luting cement interface and three depths from the outer surface of enamel and root dentin. Previous studies have reported the success of microhardness testing in caries inhibition zones adjacent to areas restored with fluoride-releasing materials.[16,28-31] The increase or decrease in hardness reflects the gain (remineralization) or loss (demineralization) of minerals in the dental structure since there is a significant correlation between Knoop hardness and the percentage of mineral.[32] Indeed, the positive correlation between the means of the cumulative fluoride release and the microhardness in enamel and root dentin demonstrates a trend between higher amounts of fluoride release and demineralization inhibition.

The measurement of mineral loss in the oral environment by *in situ* models is useful to study the anticaries potential of fluoride-releasing materials.[14,24] Because mineral loss rate can be twice as fast from the root as it is from enamel,[33] the potential of the luting cements to inhibit demineralization was accessed in both enamel and root dentin. Moreover, the fluoride delivered from dentifrices can overwhelm the anticaries effect of fluoride-releasing materials.[34] In the present study, all volunteers were instructed to use a fluoride toothpaste for their daily oral hygiene. In spite of that, the glass ionomer cement and the self-adhesive resin cements showed distinct potential in preventing demineralization on enamel and root dentin. These results do not agree with previous ones, where zinc phosphate, glass ionomer, and resin cements were not different regarding inhibitory effects on demineralization of enamel and root dentin adjacent to indirect restorations.[9,10] The absence of a high cariogenic challenge in these studies may explain this difference.

The anticaries property of restoratives is associated with the amount of fluoride released and is explained by several mechanisms, including the reduction of demineralization. Two different approaches for the development of fluoride-releasing resin materials are the addition of water-soluble salts (NaF or SnF_2) and fluoride-releasing glass filler systems. In the present study, glass ionomer cement released about 9 to 60 times more fluoride than the SARCs. Indeed, the literature shows that conventional GICs release much higher amounts of fluoride than resin-based materials.[3] A gradual dissolution of the glass particles releases fluoride continuously, creating a direct association between release and material solubility.[35-38] The inorganic filler content by weight of the SARCs declared by the manufacturers is approximately 60% to 70%. However, such range represents the amount of fluoride-containing glass fillers and other non–fluoride-containing particles. In addition, less hydrophilic matrix of resin cements probably reduced the water diffusion and the following release of fluoride from the material in contrast to the aqueous phase of GICs, which enables fluoride ions to diffuse and to be released into the media.[39]

SeT was the only SARC that resulted in enamel and root dentin hardness comparable to that of the GIC at most distances and depths. After SeT, Max resulted in hardness values comparable to GIC, but these equivalences were mainly in dentin depths that were 75 μm distant from the restoration margins. SeT and Max have fluoro-alumino-silicate glass particles that certainly released fluoride into the media following a diffusion movement down the concentration gradient as occurs in GICs. Although Smart and Unicem2 also have glass particles in their composition, these materials failed to achieve enamel and dentin microhardness values comparable to the glass ionomer cement. Smart contains strontium fluoride (SrF_2), which releases fluoride most likely by means of an exchange reaction. Sr is claimed to be beneficial in terms of potentiating the anticaries effect of F, although the optimum concentrations of these elements when combined with each other remain unclear.[40]

Mineral loss rate can be twice as fast from root dentin as it is from enamel.[33] Therefore, fluoride-containing luting resin cements could be beneficial against secondary lesions associated with indirect restorations with margins in dentin. The literature shows that GIC inhibits demineralization of enamel[14] and dentin[15] *in situ* and remineralizes these tissues under cariogenic challenge to a depth of approximately 100 μm.[20] The present study revealed a similar behavior of the materials in both enamel and root dentin. Knoop microhardness values were higher at indentations that were deeper from the outer enamel and dentin surface, probably because the pronounced effect of biofilm on the demineralization of the outer surfaces. Indentations located at a distance of 25 μm revealed higher Knoop hardness numbers than those at distances of 75 μm. Also, three of the four significant pairwise comparisons among the three highest fluoride-releasing materials (GIC, SeT, and Max) occurred at a distance of 25 μm, probably influenced by the proximity of the indentations to the fluoride-releasing cements at the margins of the restorations.

The amount of fluoride released by the glass ionomer and the self-adhesive resin cements increased when they were immersed in acid probably because of their higher dissolution under a lower pH.[41] The water/acid ratio of the materials ranged from a low of 0.047 for Max to a high of 0.310 for GIC. Similarly, a previous study with a pH-cycling regimen showed that Max exhibited higher amounts of fluoride ions in the remineralizing solution than in the demineralizing solution at the first day.[13] Differences in matrix solubility and filler particle sources between the SARCs probably explain their distinct levels of dissolution in water and acid.

Caries is a chronic disease with a daily and continuous progression. Thus, fluoride must be constantly available in the mouth to affect the disease process. An updated systematic review suggested that GIC has a higher caries-preventive effect than amalgam in margins of restorations in permanent teeth.[42] Fluoride release from luting cements may not be as effective as direct restoratives in reducing demineralization of hard tissues due to the small area of the material exposed to the oral environment. The fluoride released by the GIC was higher in the first 24 hours, which agrees with previous studies.[3,5] The initial high release is likely due to the burst of fluoride released from the glass particles that react with polyalkenoate acids during the setting reaction.[3] Then fluoride release from glass ionomers slows down and exhibits a prolonged long-term release,[43] as observed in the present study. Similar to the GIC, the amount of fluoride released from the SARCs in both media underwent a significant reduction during the 15 days of immersion. SeT, MaxCem, and Smart SARCs slow down the fluoride release until the 15th day, and the concentration measured varied from 0.17 μg F/cm^2 (Smart in water, 15th day) to 17.12 μg F/cm^2 (SeT in acid, first day). Very low concentrations of fluoride in water (0.04 μg F/cm^2) and in acid (0.09 μg F/cm^2) were detected for Unicem2 on the last day of cycling, showing that the fluoride source of this material is finite. Similarly, SARCs exposed to a pH cycling showed a gradual decrease in the fluoride release amount with time.[13]

Amounts of fluoride released *in vitro* by GICs range from 5 to 155 ppm in specimens 1 to 1.5 mm thick and 6 mm in diameter.[3] In this study, all materials, except RelyX Unicem 2, released initial amounts of fluoride that exceeded this level. Mean concentration of fluoride release from glass ionomer specimens (1.5 mm thick, 11 mm in diameter) into water/acid ranged from 99.7 to 239.1 ppm (24 hours) to 8.3 to 69.5 ppm (15th day). Fluoride release in water and acid from SeT—the SARC that most released fluoride—ranged from 19.5 to 138.0 ppm (first day) to 3.8 to 25.8 ppm (15th day). Although fluoride-releasing dental materials present the necessary properties to be effective in caries control,[34] none of the materials in the present study showed the potential to inhibit demineralization completely in both hard tissues since the Knoop hardness in all groups was below 272 to 440 KHN in enamel[44] and 55 KHN in dentin.[45] This finding agrees with the knowledge that fluoride alone reduces the development of caries but does not fully prevent its progression.[34]

CONCLUSIONS

Glass ionomer luting cement showed the highest overall potential to minimize demineralization in enamel and dentin around indirect restorations. Only one SARC (SeT) was comparable to the GIC in protecting enamel and dentin against demineralization. The GIC showed the highest cumulative fluoride release in water and acid. For GIC and SARCs, the highest fluoride release occurred on the initial days and tended to decrease with time.

Regulatory Statement

This study was conducted in accordance with all the provisions of the local human subjects oversight committee guidelines and policies of the PUCPR. The approval code for this study is 491524.

Conflict of Interest

The authors of this article certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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