Fluoride-Releasing Restorative Materials: The Effect of a Resinous Coat on Ion Release

Introduction

Glass ionomer cements (GICs), giomers, and composites are capable of releasing fluoride ions; therefore, they are used in restorative dental medicine for temporary and permanent fillings (1). Fluoride ions have been incorporated into dental materials. They have been shown to produce a remineralizing effect and reduce cariogenic potential by acting on the growth and metabolism of S. mutans (1–4).

The release of fluoride ions from dental materials depends on factors related to an individual material and factors related to oral environment. The characteristics of materials such as composition, filler content, powder/liquid ratio, mixing process, and surface exposed to the aqueous medium affect the release of fluoride ions. Environmental factors include the pH and composition of the immersion medium and application of a dental adhesive system or coat (1, 5-10).

Previous studies showed a negative effect of a dental adhesive system or coat on the quantity of released fluoride ions. Staklenionomerni cementi (SIC), giomeri i kompoziti oslobađaju fluoridne ione i zato se primijenjuju u restaurativnoj dentalnoj medicini za privremene i trajne ispune (1). Pokazalo se da dodatak fluoridnih iona u zubne materijale remineralizacijski djeluje te smanjuje kariogeni potencijal bakterija što utječe na rast i metabolizam S. mutans (1–4).

U otputstane fluoridnih iona iz dentalnih materijala ovisi o čimbenicima koji su vezani za svaki materijal te onima povezanim s oralnim okolišem. Karakteristike materijala kao što su sastav, sadržaj punila, omjer prah – tekućina, postupak mešanja i površinska izloženost vodenom mediju utječu na otpuštanje fluoridnih iona. Čimbenici okoliša uključuju pH i sastav imerzijskog medija te primjenu dentinskog adhezijskog sustava ili premaza za staklenionomerne cemente (1, 5–10). U ranijim ispitivanjima autori su istaknuli negativan učinak dentinskih adhezijskih sustava ili premaza na ukupnu količinu otpuštenih fluoridnih iona jer se smatra da tvore hi-
This has been attributed to the adhesive system or coat forming a hydrophobic barrier and thereby diminishing the diffusion of fluoride ions. This effect was more pronounced in resin composites than in GICs, which depended on type of the adhesive system or coat (7, 11-13).

Apart from the well-known classes of restorative materials that are capable of releasing fluoride ions (GICs and glass ionomers), a novel “alkasite” restorative material has recently been introduced to the dental market. This bioactive material is capable of releasing remineralizing calcium and fluoride ions and can also neutralize acid by releasing OH ions. It is compositionally similar to the group of composite materials and is designed to be used with or without an adhesive system, depending on the operator’s preferences (14, 15).

The effect of contemporary universal adhesives on fluoride release from remineralizing resin composite materials has not been investigated up to date. Therefore, the aim of this study was to compare fluoride release from specimens of restorative materials that were either coated or uncoated with a resinous layer of an adhesive system (for composite materials) and GIC (for a GIC). Additionally, the effects of a resinous layer on the pH changes of the immersion medium were investigated. The first null hypothesis was that there would be no difference in fluoride ion release and pH changes between coated and uncoated specimens. The second null hypothesis was that the release of fluoride ions and pH changes of the immersion medium did not differ among the investigated restorative materials.

**Material and methods**

Restorative materials, adhesive systems, and a glass ionomer coat investigated in this study are presented in Table 1. Six specimens were prepared for each experimental group (n = 6).

Specimens of the composite materials were prepared using cylindrical Teflon molds with a diameter of 6 mm and a height of 2 mm. The molds were placed on a polyethylene terephthalate (PET) foil, filled with uncured material and covered with another layer of PET foil (16). The excess material was removed and specimens were polymerized using an LED curing unit (Bluephase G2, Ivoclar Vivadent, Schaan, Liechtenstein) with a nominal intensity of 1200 mW/cm² for 20 s on each side. Specimens of the GIC were cast into the mold described above, covered with PET films, and left to set for 6 min according to manufacturer’s instructions (17). To ensure that the specimens were completely surrounded by an aqueous medium, a plastic thread incorporated within each specimen was used to hang the specimens from the cap of the vial.

The schematic overview of the study design is presented in Figure 1. Each sample was immersed separately in a plastic vial containing 5 ml of deionized water at 37 °C and evaluated after 0, 1, 2, 7, 28, 84, and 168 days. At each time interval, the specimens were removed from the immersion medium, placed in 5 ml of new deionized water, and stored in the incubator at 37 °C until the next time point. The pH of the immersion medium was measured using the pH meter MP 220 (Mettler Toledo, Columbus, Ohio) and the InLab Expert Pro pH (Mettler Toledo, Columbus, Ohio, SAD).

**Materijali i postupci**

Restorativni materijali, dentinski adhezijski sustavi i stakloiononemni premaz istraživani u ovoj studiji navedeni su u tablici 1. Za svaku skupinu bilo je pripremljeno šest uzoraka (n = 6).

Uzorci kompozitnih materijala pripremljeni su s pomoću cilindričnih teflonskih kalupa promjera 6 mm i visine 2 mm. Kalupi su postavljeni na polietilen-terefalatnu foliju (PET), napunjeni materijalom i prekriveni drugim slojem PET folije (16). Višak materijala je uklonjen, a uzorci su polimerizirani LED (engl. *light emitting diode*) polimerizacijskom svjetiljkom Bluephase G2 (Ivoclar Vivadent, Schaan, Liechtenstajn) nominalnog intenziteta 1200mW/cm² u trajanju od 20 sekunda sa svake strane. Uzorci SIC-a su postavljeni u kalup, prekriveni PET folijama i ostavljeni šest minuta da se stvrdnje, prema uputama proizvođača (17). Kako bi se osiguralo da su uzorci potpuno okruženi vodenim medijem, korišten je plastični konac inkorporiran u svaki uzorak, a s pomoću kojega su uzorci viseli s čepa bočice.

Schematski prikaz dizajna studije nalazi se na slici 1. Svaki uzorak bio je zasebno uvršten u plastičnu bočicu koju je sadržavala 5 ml deionizirane vode na temperaturi od 37 °C i ispitivan nakon 0, 1, 2, 7, 28, 84 i 168 dana. Pri svakom vremenskom intervalu uzorci su uklonjeni iz imerzijskog sredstva, zatim postavljeni u 5 ml nove deionizirane vode i pohranjeni u inkubator na 37 °C do sljedeće vremenske točke. pH vrijednost imerzijskog sredstva mjerila se pH metrom MP 220 (Mettler Toledo, Columbus, Ohio, SAD) i elektrodom InLab Expert Pro pH (Mettler Toledo, Columbus, Ohio, SAD).
## Materials used in this study

| Material class • Vrsta materijala | Commercial name (abbreviation) • Komercijalni naziv (kratica) | Composition • Sastav | Manufacturer • Proizvođač | Shade/LOT No. • Nijansa/LOT broj |
|-----------------------------------|-------------------------------------------------|---------------------|--------------------------|-------------------------------|
| Giomer • Beaurtifil II (BF)       | S-PRG (surface pre-reacted glass ionomer)      | Nano fillers 83.3 wt% • Nano punila 83.3 wt % | Shofu Dental GmbH, Ratingen, Germany • NJemačka | A2/051829                     |
| Alkasite • Centon (CN)            | Fillers: calcium fluorosilicate glass, Ba-Al silicate glass, Ca-Ba-Al fluorosilicate glass, Ytterbium trifluoride, Isofiller • Punila: kalcijevo fluorosilikatno staklo, Ba-Al silikatno staklo, Ca-Ba-Al fluorosilikatno staklo, itertijev trifluorid, Isofiller | Monomers: urethane dimethacrylate UDMA, Tricyclodecan-dimethanol dimethacrylate DCP, Aromatic-aliphatic-UDMA, Polyethylene glycol 400 dimethacrylate PEG-400 DMA | Ivoclar Vivadent, Schaan, Liechtenstein • Lichtenstein | A2/XL7102                     |
| Glass ionomer • Stakleni ionomer  | Fuji IX Extra (FUJ)                            | Liquid: 5-10% polybasic carboxylic acid • Tekućina: 5 – 10 % polibazična karboksilna kiselina | GC Europe, Leuven, Belgium • Belgija | A3/1801171                    |
| Conventional composite • Konvencionalni kompozit | Filtek Z250 (FIL)                              | Matrix: Bisphenol A diglycidyl ether dimethacrylate (BIS-GMA) and triethylene glycol dimethacrylate (TEGDMA), UDMA • Matrica: Bisfenol A diglicidil dimetakrilat (BIS-GMA) i trietilen-glikol dimetakrilat (TEGDMA), UDMA | 3M Deutschland GmbH, Neuss, Germany • Njemačka | A2/N984652                     |
| Universal adhesive • Univerzalni adhezivni sustav | G-aenial Bond (GB)                            | Acetone 25-50% • aceton 25 – 50 % dimethacrylate 10-20% • dimetakrilat 10 – 20 % phosphoric acid ester monomer 5-10% • monomer estera fosforne kiseline 5 – 10 % dimethacrylate component 1-5% • dimetakrilatna komponenta 1 – 5 % photoinitiator 1-5% • fotoinicijator 1 – 5 % butylated hydroxystyrene (BHT) < 0.5% • butilirani hidroksioten (BHT) < 0.5 % | GC Europe, Leuven, Belgium • Belgija | 1811281                        |
| Universal fluoride-releasing adhesive • Univerzalni adhezivni sustav koji otpušta fluoride | Clearfil Universal Bond Quick (CB)             | BIS-GMA 10-25%, ethanol 10-25%, 2-hydroxyethyl methacrylate 2.5-10%, 10-Methacryloyloxydecal dihydrogen phosphate, hydrophilic amide monomers, colloidal silica, silane coupling agent, sodium fluoride, dl-Camphorquinone, water • BIS-GMA 10 – 25 %, etanol 10 – 25 %, 2-hidroksietil metakrilat 2,5 –10 %, 10-metakriloiloksidsiel dihidrogen-fosfat, hidrofilni amidi monomeri, koloidni silicijev dioksid, silansko vezno sredstvo, natrijef fluorid, dl-kamforkinon, voda | Kuraray Europe, Hattersheim am Main, Germany • Hattersheim na Majni, NJemačka | 3L0108                        |
| Glass ionomer coat • Staklenoionomerni premaz | GC Fuji Coat LC (FC)                          | Methyl methacrylate (MMA) 25-50% • metil-metakrilat (MMA) 25 – 50 % photoinitiator 1-5% • fotoinicijator 1 – 5 % butylated hydroxytoluene (BHT) < 1% • butilirani hidroksioten (BHT) < 1 % | GC Europe, Leuven, Belgium • Belgija | 1804021                        |

Figure 1 Schematic representation of the study design.

Slika 1. Shematski prikaz dizajna studije
Coating Effect on Fluoride Release

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Normality distribution was verified using the Shapiro-Wilk's test, and equality of variances was checked using the Levene's test. Mean values of fluoride release and pH changes of the immersion medium were compared among the combinations of materials and resinous coatings using a one-way ANOVA with Tukey post-hoc adjustment. Mean values of fluoride release and pH changes of the immersion medium for each combination of materials and resinous coatings were compared among different measurement times using repeated-measures ANOVA with Bonferroni post-hoc adjustment. For all analyses, the overall level of significance was set at 0.05. Statistical analysis was performed in SPSS 20 (IBM, Armonk, NY, USA).

Results

Fluoride release

Mean concentrations of released fluoride ions from uncoated specimens are presented in Figure 2. All uncoated groups showed a statistically significant increase in released fluoride ions over time in the following order: BF < CN < FUJ. When comparing cumulative values after 168 days, FUJ demonstrated 3 times higher values than CN, and 35 times higher values than BF.

The effect of coating systems on fluoride release is shown in Table 2. The coating of composite specimens with adhesive systems led to a statistically significant decrease in the amount of released fluoride ions. Materials treated with GB released more fluoride ions than materials treated with CB. FIL released fluoride ions only when fluoride-releasing adhesive CB was applied. Both FUJ groups showed a statistically significant increase in released fluoride ions over time, whereas uncoated specimens reached 30 times higher values compared to the specimens coated with FC.

Rezultati

Otpuštanje fluoridnih iona

Srednje vrijednosti koncentracija otpuštenih fluoridnih iona iz restaurativnih materijala bez premaza prikazane su na slici 2. Svi restaurativni materijali bez premaza pokazali su statistički značajan porast otpuštenih fluoridnih iona tijekom vremena sljedećim redoslijedom: BF < CN < FUJ. Uspoređujući kumulativne vrijednosti nakon 168 dana, FUJ je pokazao tri puta veće vrijednosti od CN-a i 35 puta veće od BF-a.

Učinak premaza na otpuštanje fluoridnih iona prikazan je u tablici 2. Premazivanje kompozitnih uzoraka dentinskim adhezijskim sustavima rezultiralo je statistički značajnim smanjenjem količine otpuštenih fluoridnih iona. Materijali tretirani GB-om otpustili su više fluoridnih iona od onih tretiranih CB-om. FIL je otpustio fluoridne ione samo kada je tretiran dentinskim adhezijskim sustavom CB. Obje FUJ skupine pokazale su statistički značajni porast otpuštenih fluoridnih iona tijekom vremena te su nepremazani uzorci dosegnuli 30 puta veće vrijednosti u usporedbi s uzorcima premazanimi FC-om.
Table 2: Fluoride ions release from coated and uncoated specimens. Uppercase letters denote statistically homogeneous groups within materials subgroups (with or without coat). Lowercase letters denote statistically homogeneous materials subgroups (time points). Values are presented in ppm. Standard deviations are presented in parentheses.

Utjecaj premaza na otpuštanje fluoridnih iona

| Time (days) | Uncoated | Clearfil Universal Bond Quick | G-senial Bond | Uncoated | Clearfil Universal Bond Quick | G-senial Bond | Uncoated | Clearfil Universal Bond Quick | G-senial Bond | Uncoated | Clearfil Universal Bond Quick | G-senial Bond | Uncoated | Clearfil Universal Bond Quick | G-senial Bond | Uncoated | Clearfil Universal Bond Quick | G-senial Bond | Uncoated | Clearfil Universal Bond Quick | G-senial Bond |
|------------|----------|--------------------------------|---------------|----------|--------------------------------|---------------|----------|--------------------------------|---------------|----------|--------------------------------|---------------|----------|--------------------------------|---------------|----------|--------------------------------|---------------|----------|--------------------------------|---------------|
| 0          | 0        | 0 A                            | 0             | 0.05 (0.03) A | 0.026 (0.02) Ab | 0.01 (0.01) Ab | 0.08 (0.02) A | 0.004 (0.001) Ab | 0.005 (0.002) Ab | 2.95 (0.5) A | 0.18 (0.06) A | 0.26 (0.1) A | 2.72 (0.8) A | 0.18 (0.12) A | 0.18 (0.06) A |
| 1          | 0        | 0 A                            | 0             | 0.11 (0.05) Aa | 0.026 (0.02) Ab | 0.013 (0.01) Ab | 4.22 (0.44) Ba | 0.057 (0.02) Ab | 0.386 (0.2) Ab | 7.95 (0.89) B | 0.26 (0.1) A | 0.18 (0.12) A | 0.18 (0.06) A | 0.26 (0.1) A | 0.18 (0.12) A |
| 2          | 0        | 0 A                            | 0             | 0.14 (0.06) Aa | 0.026 (0.02) Ab | 0.013 (0.05) Ab | 7.15 (0.64) Ca | 0.071 (0.02) Ab | 0.462 (0.22) Ab | 9.94 (0.84) C | 0.18 (0.12) A | 0.18 (0.12) A | 0.18 (0.06) A | 0.26 (0.1) A | 0.18 (0.12) A |
| 7          | 0        | 0.0000833 A                    | 0             | 0.22 (0.07) Aa | 0.025 (0.02) Ab | 0.016 (0.04) Ab | 8.93 (0.75) Da | 0.08 (0.03) ABCb | 0.91 (0.33) Ac | 14.5 (0.56) D | 0.61 (0.25) A | 0.18 (0.12) A | 0.18 (0.06) A | 0.26 (0.1) A | 0.18 (0.12) A |
| 28         | 0        | 0.000695 B                     | 0             | 0.6 (0.16) Bx | 0.16 (0.1) Aa | 0.087 (0.01) Ab | 10.12 (0.99) DEa | 0.23 (0.05) BcB | 2.669 (0.72) Bc | 22.49 (1.16) E | 0.93 (0.33) BC | 0.18 (0.12) A | 0.18 (0.06) A | 0.26 (0.1) A | 0.18 (0.12) A |
| 84         | 0        | 0.0007666 B                   | 0             | 1.01 (0.26) Ca | 0.08 (0.03) Bb | 0.322 (0.07) Bc | 10.8 (1.06) Ea | 0.24 (0.05) Cb | 3.088 (0.69) Bc | 45.7 (2.12) F | 0.18 (0.12) A | 0.18 (0.06) A | 0.26 (0.1) A | 0.18 (0.12) A |
| 168        | 0        | 0.0007666 B                   | 0             | 2.19 (0.43) Da | 0.08 (0.03) Bb | 1.77 (0.17) Bc | 12.75 (1.07) Fa | 0.80 (0.23) Db | 5.072 (0.99) Cc | 55.49 (3.0) G | 1.85 (0.5) D | 0.18 (0.12) A | 0.18 (0.06) A | 0.26 (0.1) A | 0.18 (0.12) A |

Table 3: pH changes in coated and uncoated groups. Uppercase letters denote statistically homogeneous groups within materials subgroups (with or without coat). Lowercase letters denote statistically homogeneous materials subgroups within time points. Values are presented in ppm. Standard deviations are presented in parentheses.

pH changes

The pH of dental materials differed in the first measurement (1 h time point) in the following order: FIL < FUJ < CN < BF (6.16, 6.47, 6.83, and 7.26). Also, the values differed at the last measurement (168 days): FUJ < FIL < CN < BF (6.56, 6.63, 6.91, and 7.45).

pH values in coated and uncoated specimens are presented in Table 3. pH values showed growth tendency over time.
in all tested materials. FIL and CN showed higher pH values when coated with CB than the uncoated group. BF showed the highest values in the uncoated group. FUJ showed higher values when coated with FC. GB showed lower pH values in all groups after 1 hour and 24 hours. After 1 hour, the pH values among the materials increased in the following order: FIL < CN < BF (4.42, 4.53, and 4.75). After 24 hours, the pH values increased among the materials in the following order: FIL < BF < CN (5.39, 5.67, and 5.73).

**Discussion**

This study investigated fluoride release of four restorative materials and the effect of contemporary universal adhesive systems, and a coat on fluoride ions release. Also, for all coat-
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ed and uncoated specimens, pH changes were evaluated. According to a statistically significant effect of the material type and resinous coating on fluoride release and pH changes, both null hypotheses were rejected.

All fluoride-releasing materials used in this study showed long-term fluoride release, as reported in several previous studies (18, 19). FUJ presented the highest cumulative values of released fluoride ions, followed by CN and BF. As expected, the conventional composite FIL did not release fluoride ions, except when its specimens were coated with the fluoride-releasing adhesive CB.

GICs are characterized by the initial release of a large amount of fluoride ions called the burst effect which occurs within 24 h of cement setting time (20-22). According to Wiegand et al., this effect results from a reaction between glass particles and polyalkenoate acid (1).

Our study confirmed a similar burst effect in FUJ specimens, and also in the alkasite composite material CN. However, the burst effect was present only in uncoated FUJ and CN specimens. The observed burst effect found in CN could be a result of its composition. According to the respective manufacturer, this material comprises 78.4 wt% of the following inorganic fillers: barium aluminum silicate glass, ytterbium trifluoride, Isosfiller (patented filler), calcium barium aluminum fluoride silicate glass, and a calcium fluorosilicate (alkaline) glass. Also, 24.6 wt% of the material is composed of alkaline (calcium fluoride silicate) glass filler, which is responsible for fluoride, hydroxide, and calcium ions release (14).

Our results are partially in contrast with those from a study of Gupta et al., which tested similar materials, Cen-tion N (self- and light-cured) and a conventional GIC. Their results showed a time-dependent decrease in fluoride release from all tested materials, except for GIC in an acidic immersion medium. This difference between the released fluoride ions could be a result of different measuring time periods in the aforementioned study (7, 21, and 28 days). However, their results of a GIC in neutral medium releasing significantly higher amounts of fluoride ions than Cen-tion N corroborate our results of fluoride ions release in these materials (23).

Tiskaya et al. evaluated fluoride release, pH changes, and apatite formation of two bioactive composites (Cen-tion N and Activa). Their cumulative values of fluoride ions release were below 8 ppm after 42 days, which is lower than the values obtained in our study (30.49 ppm after 28 days). This difference could be due to different specimen geometry and different immersion media. In our study, specimens were stored in deionized water while artificial saliva was used in the aforementioned study. Specimens immersed in artificial saliva tend to show a 17–25% lower fluoride release compared to specimens immersed in water (24, 25). This is explained by a lower diffusion gradient between the material and artificial saliva compared to the diffusion gradient between the material and deionized water. Also, artificial saliva may contain components that form a pellicle on the material surface and thereby interfere with ion release, decreasing it for about 15-20% (1, 25-27).

na otpuštanje fluoridnih iona. Također su se za sve prema-zane i nepremazane uzorke pratile promjene pH vrijednosti imerzijskog sredstva. Prema utvrđenom statistički značajnom učinku vrste materijala i premaza na otpuštanje fluoridnih io-ni i promjene pH, sve nulte hipoteze su odbačene.

Svi materijali koji otpuštaju fluoridne ione korišteni u ovoj studiji pokazali su dugotrajno otpuštanje fluorida, kao-ko je navedeno i u nekoliko ranijih studija (18, 19). Najviše kumulativne vrijednosti otpuštenih fluoridnih ioni imali su uzorci FUJ-a, zatim slijede CN i BF. Očekivano, konvencionalni kompozit FIL nije otpuštio fluoridne ione, osim u skupini premazanoj dentinskim adhezijskim sustavom CB koji ima svojstvo otpuštanja fluoridnih ione.

Staklenoionomerne cemcrete karakteriziraju početno otpuš-tanje velike količine fluoridnih ioni pod nazivom burst effect koji se pojavljuje unutar 24 sata od početka vezivanja cemen-ta (20 – 22). Prema Wiegandu i suradnicima, navedeni uči-nak rezultat je reakcije između čestica stakla i polialkenoat- ne kiseline (1).

U ovom istraživanju potvrđen je burst effect kod FUJ uzor-aka, a i u alkasitnom kompozitnom materijalu CN. No uči-nak se pojavio samo u uzorcima FUJ i CN pripremljenima bez premaza. Uočen efekt pronaden u CN-u mogao bi biti rezultat njegovog sastava. Kako navodi proizvođač, taj materijal sadržava 78,4 % težinskog udjela sljedećih anorganskih punila: barij-aluminijeva silikatnog stakla, iterebijeva trifluo- rida, Isosfillera (patentirano punilo), kalcij-barij-aluminijeva fluorosilikatnog stakla i kalcijeva fluorosilikata (alkalno stak- klo). Također se 24,6 % težinskoga udjela materijala sasto- ji od alkalnoga (kalcijeva fluorosilikatnog) staklenog punila odgovornog za otpuštanje fluoridnih, hidrokislinskih i kalcije- vih ione (14).

Rezultati u ovoj studiji djelomično su u suprotnosti s onima iz studije Gupta i suradnika koji su testirali slične materijale, Cen-tion N (kemijski polimerizirani i svjetlosno polimerizirani) i konvencionalni SIC. Njihovi su rezulta-ti pokazali vremenski ovisno smanjenje otpuštanja fluoridnih iona iz svih ispitivanih materijala, osim SIC-a u kiselom imerzijskom mediju. Ta razlika između otpuštenih fluoridnih iona mogla bi biti rezultat različitih razdoblja mjerenja u spomenutoj studiji (7, 21 and 28 dana). No njihovi rezulta-ti uzoraka SIC-a u neutralnom mediju koji otpuštaju znatno- no veće količine fluoridnih ioni od Cen-tion N, potvrđuju naše rezultate o otpuštanju fluoridnih ioni u tim materija-lima (23).

Tiskaya i suradnici proučavali su otpuštanje fluoridnih ioni, promjene pH i stvaranje apatita dvaju bioaktivnih kompo-zita (Cen-tion N i Activa). Njihove kumulativne vrijednosti otpuštanja fluoridnih ioni bile su manje od 8 ppm nakon 42 dana, što je niže od vrijednosti dobivenih u našem istraživa-nju (30,49 ppm nakon 28 dana). Ta razlika može biti posljedica različite geometrije uzorka i različitih imerzijskih medija. U našem istraživanju uzorci su bili pohranjeni u deioniziranoj vodi, a u spomenutom istraživanju korištena je umjetna slina. Uzorci urojeni u umjetnu slinu pokazuju od 17 do 25 % niže vrijednosti otpuštenih fluoridnih ioni u usporedbi s uzorcima urojenima u deioniziranoj vodi (24, 25). Smatra se da je to rezultat nižeg gradijenta difuzije između materija-
The gionomer BF did not show the burst effect, which is in correspondence with the study of Yap et al. (28). The slower release of fluoride ions from BF can be attributed to its hydrophobic resinous matrix and a relatively low amount of pre-reacted glass ionomer fillers. Similar to the findings of our study, Mousavinasab et al. have also reported a higher release of fluoride ions from a GIC compared to a gionomer. According to their study, the differences in fluoride ions release between those materials could be caused by a greater porosity of GIC, lack of glass ionomer matrix phase, and incorporated resin components in gionomers (29).

In our study, the gionomer showed the lowest cumulative fluoride release. According to a study by Colceriu Burtea et al., this finding can be explained by material characteristics where gionomers include polyacrylic acid from PRG (pre-reacted glass) rather than amino acid modified polyalkenoic acid in the composition of the PRG. They also found that experimental gionomers which contained hydrophilic and flexible polymer matrix based on UDMA showed higher cumulative fluoride ions release than gionomers based on rigid and hydrophobic dimethacrylates (TEGDMA in BF) (1, 19, 28, 30).

The results of our study showed that the amount of released fluoride ions in all investigated materials was diminished in coated specimens, which is in line with previous studies (7, 11, 12). Surprisingly, the fluoride-releasing adhesive system reduced the amount of leached fluoride ions.

In the present study, the materials coated with GB showed higher fluoride ions release than materials coated with the fluoride-releasing adhesive system CB. This could be explained by material composition. Water sorption depends on material hydrophilicity and can reduce polymer mechanical properties affecting its hydrothermal degradation and polymer hydrolysis that later forms water channels, surface erosions, and crazing that impact material permeability (31–34). High concentrations of acidic monomers contribute to hydrophilicity. GB contains 5-10% phosphoric acid ester monomers, while CB contains hydrophilic amid monomers (35, 36). Resin monomers with ester bonds are highly prone to hydrolysis in the presence of water, which could be one of the reasons for an increased fluoride ions release from materials coated with GB (37, 38). Also, some studies found that resin polarity can act as a major determinant of water uptake. An increase in polarity results in higher water sorption. Polar functional groups include OH- groups, carboxyl groups and phosphate groups, which tend to form hydrogen bonds with water. The water molecules that are „bound“ by polar functional groups induce swelling and plasticization of the polymer network (31, 39–41). The GB adhesive system used in this study had dimethacrylate (10–20%) and dimethacrylate components (1–5%). Those components could partially explain an increased amount of released fluoride ions from materials coated with GB.

The hydrophilic resins used in universal adhesive systems are prone to limited monomer conversion due to phase separation which leads to degradation in an aqueous medium (38, 42). Oguri et al. showed that degree of conversion could depend on the functional monomer and photoinitiator system (43). Also, the lack of compatibility between hydropho-

la and umjetne sline uusporedbi s gradijentom difuzije između materijala i deionizirane vode. Umjetna slina također može sadržavati komponente koje tvore pelikulu na površini materijala i tako ometaju otpuštanje iona, smanjujući ga za oko 15 do 20 % (1, 25 – 27).

Gionomer BF nije pokazao burst effect, što je u skladu sa istraživanjem Yapa i suradnika (28). Sporije otpuštanje fluoridnih iona iz BF-a može se pripisati njegovoj hidrofobnoj smolasti matrici i razmjetno maloj količini prethodno reagiranih staklenoionomernih čestica punila. Slično našem istraživanju, Mousavinasab i suradnici također su izvijestili o većem otpuštanju fluoridnih iona iz SIC-a u usporedbi s gioneromom. Prema njihovu istraživanju, razlike u otpuštanju fluoridnih iona između materijala mogle bi biti prouzročene većom poroznošću SIC-a, nedostatkom matrične faze i ugраđenim komponentama smole u gioneru (29).

U našoj studiji gionomer je pokazao najnižu kumulativno otpuštanje fluoridnih iona, a prema studiji Colceriu Burteae i suradnika te se vrijednosti mogu objasniti karakteristikama materijala u kojima gionomeri uključuju poliakrilinu kiselinu iz PRG-a, a ne modificiranu aminokiselinu polialkenoatne kiseline u sastavu PRG-a. Također su otkrili da su eksperimentalni gionomeri koji su sadržavali hidrofilnu i fleksibilnu polimernu matricu na bazi UDMA-e pokazivali veće kumulativno otpuštanje fluoridnih iona od gionera na bazi krutih i hidrofobnih dimetakrilata (TEGDMA u BF-u) (1, 19, 28, 30). Rezultati ovog istraživanja pokazali su da je količina otpuštenih fluoridnih iona u svim ispitivanim materijalima bila niža u premazanim uzorcima, što je u skladu s ranijim studijama (7, 11, 12). Izmenačuje se da je dentinski adhezijski sustav koji otpušta fluoridne ione smanjio količinu otpuštenih fluoridnih iona.

U ovom istraživanju su materijali premazani GB-om pokazali veće otpuštanje fluoridnih iona od onih premazanih adhezijskim sustavom CB koji ima svojstvo otpuštanja fluoridnih iona. Dobiveni rezultat mogao bi se objasniti sastavom materijala. Sorpcija vode ovisi o hidrofilnosti materijala i može smanjiti mehanička svojstva polimera tako što utječe na njegovu higrotermalnu razgradnju i hidrolizu polimeru koja poslije stvara vodene kanale, površinske erozije i pukotine koje utječu na propusnost materijala (31–34). Visoka koncentracija kiselim monomerima pridonosi hidrofilnosti, CB sadržava od 5 do 10 % monomerima estera fosforne kiseline, a CB pak monomer hidrofilnih amida (35, 36).

Monomeri smole s esterskim vezama vrlo su skloni hidrofilnosti i prisutnosti vode, što bi mogao biti jedan od razloga za povećano otpuštanje fluoridnih iona iz materijala premazanih adhezijskim sustavom GB (37, 38). Također je u nekim istraživanjima otkriveno da polaritet smole može djelovati kao glavna odrednica sorpcije vode. Što je smola polarnija, to je veća sorpcija vode. Polarne funkcionalne skupine uključuju OH- skupine, karbonske skupine i fosfatne skupine koje imaju tendenciju stvaranja vodikovih veza s vodom. Moleku
e vode koje su „ vezane“ polarnim funkcionalnim skupinama izazivaju bubrenje i plastificiranje polimerne mreže (31, 39 – 41). Dentinski adhezijski sustav GB korišten u ovom studiji u svojem sastavu ima dimetakrilat (10 – 20 %) i dimetakrilatne komponente (1 – 5 %). Te bi komponente mogle djelomić-
bic photoinitiator and hydrophilic monomers showed lower values of degree of conversion when compared with hydrophilic photoinitiator and monomers. A lower degree of conversion can affect adhesive permeability and lead to acidic monomer diffusion (44-46). CB scientific documentation declares the presence of hydrophobic photoinitiator camphorquinone and hydrophilic amide monomers which could explain lower pH values than pH values in uncoated specimens after 1 hour for BF and FIL, and after 24 hours for CN (35). A lower degree of conversion can also be speculated to have led to lower pH values for GB at time intervals 1 hour and 24 hours.

According to its respective manufacturer, CN shows a buffering ability by releasing acid-neutralizing hydroxide ions. Our results demonstrated small pH changes when CN was exposed to neutral medium, which can be compared with the studies of Gupta et al. and Tiskaya et al. (23, 24). Also, an interesting finding from our study was that the average pH level for CN was higher in the group that was coated with CB compared with the uncoated group. A similar result was present for FIL, but not for BF, and this could be due to increased reactivity when the acidic coat was applied.

FUJ also presented higher pH values when coated with FC. Given that uncoated FUJ specimens tended to decrease the pH value from neutral to acidic over time, the barrier formed in coated specimens showed a lack of that tendency.

GB showed lower pH levels than uncoated specimens and coated with CB. This can be related with a higher concentration of released fluoride ions when compared with materials coated with CB adhesive. The results of similar studies showed that the highest fluoride ions release was found in acidic medium (23, 47-49).

Conclusions

The amount of released fluoride ions varied among dental materials and depended on the use of adhesive systems and coatings. The glass ionomer Fuji IX Extra showed the highest values of released fluoride ions followed by the alka- site material Cention and the giomer Beautifil II. Both adhesive systems and the coat had a diminishing effect on released fluoride ions. pH values of the immersion medium differed among materials, treatments and time points. The amount of released fluoride ions showed a growth tendency over time in all tested materials. The lowest pH values were identified in all material specimens coated with G-aenial Bond.

no objasniti povećanu količinu otpuštenih fluoridnih iona iz materijala premazanih GB-om.

Hidrofiline smole koje se koriste u univerzalnim dentin- skim adhezijskim sustavima sklene su ograničenoj konverziji monomera zbog razdvajanja faza, što potiče razgradnju u vodenom mediju (38, 42). Oguri i suradnici pokazali su da stupanj konverzije može ovisiti o funkcionalnom monome- ru i sustavu fotoiniciatora (43). Nedostatak kompatibilnosti između hidrofobnog fotoiniciatora i hidrofobnih monomera također je pokazao nižu vrijednost stupnja konverzije u uspo- redbi s hidrofobnim fotoiniciatorom i monomerima. Niži stupanj pretvorbe može utjecati na propusnost adhezijskog su- stava i rezultirati difuzijom kiselog monomera (44 – 46). U znanstvenoj dokumentaciji o CB-u navodi se prisutnost hidrofobnog fotoiniciatora kamforkinona i hidrofobnih amidnih monomera koji bi mogli objasniti niži pH vrijednosti od pH vrijednosti na nepremazanim uzorcima nakon jednog sa- ta za BF i FIL, te nakon 24 sata za CN (35). Također se može pretpostaviti da je niži stupanj konverzije doveo do nižih vrijednosti pH kod uzoraka premazanih GB-om u vremenskim razmacima od jednoga sata i 24 sata.

Prema proizvođaču, CN pokazuje pufersko svojstvo ot- puštanjem hidroksidnih iona koji neutraliziraju kiselinu. Na- ši rezultati pokazali su male promjene pH kada je CN bio izložen neutralnom mediju i mogu se usporediti sa studijama Gupta i suradnika te Tiskaya i suradnika (23, 24). Također je zanimljivo otkriće u našoj studiji bilo da je prošječna razi- na pH za CN bila viša u skupini premazanoj CB-om nego- li u onoj nepremazanoj. Sličan rezultat dobiven je za FIL, ali ne i za BF, a to bi moglo biti zbog povećane reaktivnosti ka- da se nanese kiseli sloj.

FUJ je također pokazao veće pH vrijednosti kod uzoraka premazanih FC-om. S obzirom na to da su uzorci FUJ-a bez premaza s vremenom smanjivali pH vrijednost s neutralnog na kiseli, barijera nastala u premazanim uzorcima onemogu- čila je spomenutu pojavu.

GB je pokazao nižu razinu pH vrijednosti od neprema- zanih uzoraka i uzoraka premazanih CB-om. Navedeni re- zultat može se povezati s većom koncentracijom otpuštenih fluoridnih iona u usporedbi s materijalima premazanim CB adhezivom. U sličnim je istraživanjima istaknuto da se najve- će otpuštanje fluoridnih iona događa u kiselim mediju (23, 47 – 49).

Zaključak

Količina otpuštenih fluoridnih iona varirala je među den- talnim materijalima i ovisila je o tome u kojem se sustavu adhezijskog sustava koristi the glass ionomer. Stakleni ionomer Fuji IX Extra pokazao je najveće vrijednosti otpuštenih fluoridnih iona, a slijedili su ga alkasitni materijal Cention i giomer Beautifil II. Dentinski adhezijski sustavi u premazu manjši su subjektivno u usporedbi s fluoridnim ionima. Vrijednosti pH imerzijskog sredstva razliko- vale su se između materijala, tretmana i vremenskih točaka. Količina otpuštenih fluoridnih iona pokazala je tendenciju rasta tijekom vremena u svim ispitivanim materijalima. Naj- niže pH vrijednosti utvrđene su u svim uzorcima materijala premazanima G-aenial Bondom.
Conflict of interest

The authors report no conflict of interest.

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Author’s contribution

K.K. - research, data collection, formal analysis, interpretation, visualization, writing - original draft, approval of the final version of the article for publication; M.P. - concept and design, formal analysis, statistical analysis, interpretation, writing - critical review and editing, approval of the final version of the article for publication; K.P. - concept and design, supervision, interpretation, writing - critical review and editing, approval of the final version of the article for publication; I.Š. - concept and design, supervision, interpretation, writing - critical review and editing, approval of the final version of the article for publication; Z.T. - supervision, resources, writing - critical review and editing, approval of the final version of the article for publication.

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Autori nisu bili u sukobu interesu.

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