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Otpuštanje fluorida iz materijala za nadoknadu tvrdih zubnih tkiva

Fluoride Release from Hard Dental Tissue Restorative Materials

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Sažetak
Svrha: Ovim istraživanjem *in vitro* željelo se utvrditi i usporediti razinu i dinamiku otpuštanja fluorida u trima najnovijim materijalima za ispune. **Materijali i postupci:** Otpuštanje fluorida mjerilo se u kompozitu *GC Kalore*, staklenom ionomernom cementu *GC Equia* i giomeru *Shofu Beautifil II*. Od svakog materijala pripremljeno je 20 diskova (promjera 8 mm, debljine 2 mm). Mjerenje se obavljalo 10 tjedana ion-selektivnom elektrodom (ORION EA 940). Za statističku obradu dobivenih rezultata odabrana je metoda linerane regresije. **Rezultati:** Kompozit *GC Kalore* otpustio je 1,29 ppm F^- tijekom 10 tjedana ispitivanja. Otpuštanje fluorida smanjilo se i nakon četiri tjedna više se nije moglo izmjeriti ion-selektivnom elektrodom. Stakleni ionomerni cement *GC Equia* otpustio je najviše fluoridnih iona (24,512 ppm F^-) i to u prva 24 sata (6,851 mgF^-/L). Giomer *Shofu Beautifil II* otpustio je 4,685 ppm F^-. **Zaključak:** Ispitivani giomer otpustio je više fluorida od kompozitnog materijala i zato se može preporučiti kao materijal izbora za estetske ispune kod kojih je važan i preventivni učinak na karijes.

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Ključne riječi
kompozitne smole; stakleno-ionomerni cementi; fluoridi; giomer

Uvod

Fluoridima se već desetljećima prevenira karijes zahvaljujući sustavnoj, endogenoj fluoridaciji (fluoridacija pitke vode, kuhinjske soli, mlijeka i primjena tableta s fluorom) i topikalnoj, lokalnoj fluoridaciji u obliku otopina, želea, lakova i pjene (1,2). Tako fluoridi u zubnim pastama omogućuju svakodnevnu izloženost malim koncentracijama fluorida, što se smatra važnim čimbenikom u smanjenju prevalencije karijesa u razvijenim zemljama (3).

Posljednjih desetljeća njihovo dodavanje u restaurativne materijale privuklo je pozornost kliničara i istraživača jer je uočeno da ti materijali dulje mogu otpuštati male količine fluorida. Primijećeno je da tzv. pametni dentalni materijali smanjuju karijes i neutraliziraju snižavanje pH vrijednosti, posebice ako je osoba izvrgnuta velikom riziku od karijesa (4). Njihova mehanička i estetska svojstva poboljšana su, te se danas se mogu rabiti za ispune stražnjih zuba, a neki i za ispune prednjih (4).

Fluoridi koji se oslobađaju iz restaurativnih materijala djeluju na karijesnu leziju tako da smanjuju i sprječavaju demineralizaciju i potiču remineralizaciju tvrdih zubnih tkiva (5).

Introduction

For decades, fluorides have been used in caries prevention through systemic, endogenous fluoridation (potable water fluoridation, kitchen salt as well as milk fluoridation and the use of fluoride containing pills) as well as through topical, local fluoridation, that is, by solutions, gels, tooth polishes and foams (1, 2). The presence of fluoride in tooth pastes enabling the everyday exposure to small concentrations of fluoride is considered an important factor in reducing the caries prevalence which has been noted in developed countries (3).

In the last decades, adding fluorides to restorative materials drew attention from clinicians and researchers since there is a possibility that these materials release small quantities of fluorides during longer time periods. It has been observed that the so-called smart dental materials reduce the incidence of dental caries and neutralize the reduction of pH value, particularly in high caries risk individuals (4). Their mechanical and esthetic properties have been enhanced and today they are used for fillings of the posterior teeth and some of them for fillings of anterior teeth (4).

Danas je na tržištu nekoliko vrsta materijala koji otpuštaju fluoride, a primjenjuju se u restaurativnoj stomatologiji za trajne ispune. To su stakleni ionomerni cementi, kompomeri, kompozitni materijali i amalgami. Toj skupini odnedavno su se priključili giomeri – hibridi staklenih ionomera. Zbog različitog sastava i načina stvrdnjavanja ti se materijali razlikuju prema svojstvu otpuštanja fluorida. Pretpostavlja se da su antibakterijske i kariostatske mogućnosti ispuna izravno povezane s količinom otpuštenih fluorida (5).

Svrha ovog istraživanja bila je odrediti i usporediti otpuštanje fluorida iz staklenog ionomernog cementa i kompozitnog materijala novije generacije te giomera. Također se željela proučiti dinamika otpuštanja navedenih iona i utvrditi postojanje tzv. *burst* ili intenzivnog učinka.

Materijali i postupci

U istraživanju je testirano otpuštanje fluoridnih iona iz kompozitnog materijala, staklenog ionomernog cementa i giomera prikazano u tablici 1. Od svakog od njih izrađeni su diskovi (20 komada za svaki materijal). Svi su približno iste veličine koja debljinom i veličinom odgovara prosječnoj veličini trajnog ispuna. Za izradu smo se koristili standardiziranim metalnim obručima promjera osam milimetara i debljine dva milimetra u koji su se stavljali navedeni materijali. Kompozitni materijal i giomer na staklenoj su se pločici plastičnim instrumentom stavljali u metalne prstene te polimerizirali 20 sekundi polimerizacijskim svjetlom Woodpecker LED.B 5W (Guangxi, Kina). Kapsulirani ispitivani stakleni ionomerni cement je zatim unesen u metalni prsten pištoljem koji se rabi za njegovo nanošenje, a prije toga je aktiviran i pomiješan u amalgamatoru. Kako bi uzorci tijekom ispitivanja bili slobodni na svim površinama s kojih se mogu oslobađati fluoridi, prije polimerizacije materijala u sredinu uzorka utisnuta je nit zubnog konca bez fluorida, a nakon toga je polimeriziran.

Uzorci su nakon toga izvagani, a zatim pohranjeni u plastične bočice i uronjeni u pet mililitara deionizirane vode. Tako pripremljeni čuvali su se u termostatu na temperaturi od 37°C. Količine otpuštenih fluorida izmjerene su nakon 6 sati, 24 sata i 48 sati, te nakon jednog, dva, četiri, sedam i deset tjedana. Ova vremenska razdoblja odabrana su zato da bi se rezultati lakše usporedili s podacima drugih autora. Kvantitativno otpuštanje fluorida ispitivalo se standar-

Fluorides which are released from restorative materials affect the carious lesion by reducing or preventing demineralization of hard dental tissues or by stimulating their remineralization (5).

Currently, several kinds of materials which release fluorides are available on the market and used in restorative dentistry for permanent fillings which release fluorides. These are glass ionomer cements, compomers, composite materials and amalgams. Recently, giomers – hybrids of glass ionomers – were added to that group of materials. Due to their different compositions and modes of hardening, these materials vary in their ability to release fluorides. It is assumed that antibacterial and cariostatic properties of the fillings are directly correlated with the amount of released fluorides (5).

The aim of this study was to determine and compare the release of fluorides from glass ionomer cements and composite materials of new generation as well as giomers. Also, this study aimed at studying the dynamics of the above mentioned ion release, that is, determining the existence of the so-called "burst" effect.

Materials and methods

The study investigated the release of fluoride ions in composite material, glass ionomer cement and giomer shown in Table 1. Discs were fabricated from each material (20 pieces for each material).

All the discs were made in such a way to be of approximately equal size, the thickness and size of which matched an average size of a permanent filling. In order to fabricate the discs, standardized metal rings 8 mm in diameter and 2 mm thick were used and the above mentioned materials were placed in them. The composite material and the giomer were placed into the metal rings on a glass plate by a plastic instrument and were light-cured for 20 seconds using Woodpecker LED.B 5W light (Guangxi, China). The tested capsulated glass ionomer cement was placed into the metal ring by an applicator gun after it had been activated and mixed in the amalgamator. In order to make the samples free on all surfaces from which fluorides could be released during testing, prior to light-curing of the material, a thread of dental floss without fluorides was pressed into the middle of the sample.

The samples were then weighed. After that, they were immersed and stored in plastic bottles with 5 ml of deionized water. Samples prepared in this way were stored in a thermostat at 37°C. The quantities of released fluorides were measured in the following time periods: after 6 hours, 24 hours, 48 hours and after 1, 2, 4, 7 and 10 weeks. Those time periods were chosen for easier comparison of results with similar data investigation of other authors. The quantitative fluoride

Tablica 1. Materijali korišteni u ovom ispitivanju
Table 1 Materials used in this investigation

Skupina A • Sample A	Skupina B • Sample B	Skupina C • Sample C
Kompozitni materijal • composite material GC Kalore GC Europe NV, Leuven tuba, boja A2 • tube, shade A2	Stakleni ionomerni cement • glass ionomer cement GC Equia GC Europe NV, Leuven kapsula, boja A2 • capsule, shade A2	Giomer • giomer Shofu Beautifil II SHOFU, San Marcos, USA tuba, boja A2 • tube, shade A2

dnom metodom – ion-selektivnom elektrodom za mjerenje koncentracije fluorida (fluoridna ion-selektivna elektroda tipa 96-09, Boston, Mass, SAD) i mikroprocesorskim analizatorom ORION EA 940 (Orion Res Inc, SAD). To je metoda kojom se elektrokemijski (potenciometrijski) određuje količina fluorida i danas se smatra najprihvatljivijom za određivanje otpuštanja fluorida u neki medij (6). Tijekom mjerenja svaki je uzorak izvađen iz deionizirane vode, ispran deioniziranom vodom, osušen na papirnatom ubrusu te stavljen u novu, svježe pripremljenu deioniziranu vodu.

Pri mjerenju uređaj je ponovno kalibriran za svaku skupinu materijala. Svaki je uzorak mjeren tri puta. Prije mjerenja količine fluorida provjerena je ispravnost mjernog instrumenta i nagib elektrode prema uputi proizvođača. Količina otpuštenih fluorida mjerila se izravno, u triplikatu za svaki uzorak. Svi su uzorci miješani jednakom brzinom magnetskim mješačem i magnetskim štapićem. Između miješalice i posude stavljen je komadić stiropora (debljine 5 mm) kako se tijekom mjerenja ne bi promijenila temperatura otopine, što bi moglo utjecati na rezultate. Samo mjerenje sastojalo se od standardnog baždarenja. Fluoridni standardi priređeni su serijskim razrjeđenjem komercijalnog standarda (0,1 mol otopina natrijeva fluorida Orion 940906). Svaki uzorak i standard pomiješan je u količini od 4, 5 mL s 0,5 mL pufera (TISAB III (Merck KGaA, Darmstadt, Njemačka). Rezultati su izraženi u mg/L (ppm).

Dobiveni podaci obrađeni su metodom linearne regresije koju su Can Karabulut i njegovi suradnici preporučili kao najbolju za ispitivanje materijala koji otpuštaju fluoride (7). U analizi podataka korišten je statistički program The Statistical Package for Social Science 10.1.4 (SPSS Inc. Chicago, III., SAD). Za testiranje matematičkih izračuna korištena je mrežna stranica: www.wolframalpha.com (8). Izračunati su srednja vrijednost, standardna devijacija i kumulativno otpuštanje fluorida tijekom vremena izraženog u satima ($p=0,05$).

Rezultati

Logaritamske vrijednosti otpuštenih fluoridnih iona izmjerenih u ispitivanom vremenu u uzorcima A, B i C nalaze se na slici 1. Uzorci A, B i C otpuštali su fluoridne ione u logaritamskoj ovisnosti s vremenom. (Uzorak A: $y=0,2556Ln(x)-0,5713$; uzorak B: $y=4,0737Ln(x)-5,0637$; uzorak C: $y=0,9183Ln(x)-1,9826$)

Srednja vrijednost i standardna devijacija uzoraka nalaze se u tablici 2.

Uzorak A je u ukupno 10 tjedana ispitivanja otpustio 1,294 mgF^-/L. Najviše fluoridnih iona otpustilo se u prvih 200 sati. Dinamika otpuštanja u uzorku A prikazana je na slici 2. Na početku ispitivanja dinamika otpuštanja fluoridnih iona bila je mnogo veća nego poslije. U prvih šest sati bilo je najviše otpuštenih fluoridnih iona po satu – čak 0,009 mgF^-/L. Nakon prvog tjedna dinamika se jako smanjivala, a nakon četiri tjedna otpuštanje iona bilo je gotovo zanemarivo.

release was tested by a standard method using ion-selective electrode for measuring the concentration of fluorides: fluoride ion-selective electrode type 96-09 (Boston, Mass, SAD) and microprocessor analyzer ORION EA 940 (Orion Res Inc, USA). This is the method of electrochemical (potentiometric) determination of fluoride releasing ions which is nowadays considered to be the most acceptable method for measuring of fluoride ions release in certain media (6). During the measuring, each sample was taken from the deionized water, rinsed with deionized water, dried on the paper tissue and placed into new, fresh deionized water.

On measuring, the device was recalibrated for each group of materials. Three measurements were performed for each sample. Prior to measurements of the fluoride quantities, the accuracy of the measuring instrument was checked as well as the electrode inclination according to the manufacturer's instructions. The quantity of released fluorides was measured directly, in triplicate for each sample. During the measuring, all samples were stirred at equal speed by means of magnetic stirrer and magnetic stir bar. A piece of Styrofoam (5 mm thick) was placed between the stirrer and the vessel in order to maintain the temperature during the measuring period which could affect the results of measuring. The actual measuring consisted of standard method of calibration. Fluoride standards were prepared by serial diluting of commercial standard (0.1 mol sodium fluoride solution, Orion 940906). Each sample and standard was mixed in the quantity of 4.5 mL with 0.5 mL of buffer TISAB III (Merck KGaA, Darmstadt, Germany). The results of measurements were expressed in mg/L (ppm).

The obtained data were processed by the method of linear regression analysis, which was recommended by Can Karabulut et al. as the best method for investigation of fluoride releasing materials (7). Statistics were made using the statistical software Statistical Package for Social Sciences (SPSS) for Windows ver. 10.1.4 (SPSS Inc. Chicago, III., USA). The www.wolframalpha.com website was used for testing of results of mathematical calculations (8). Mean, standard deviation and cumulative fluoride release over time were calculated and showed per hour ($p=0.05$).

Results

Logarithmic values of released fluoride ions measured in determined time periods in samples A, B and C are shown in Figure 1.

Samples A, B and C released the fluoride ions in logarithmic dependence on time.

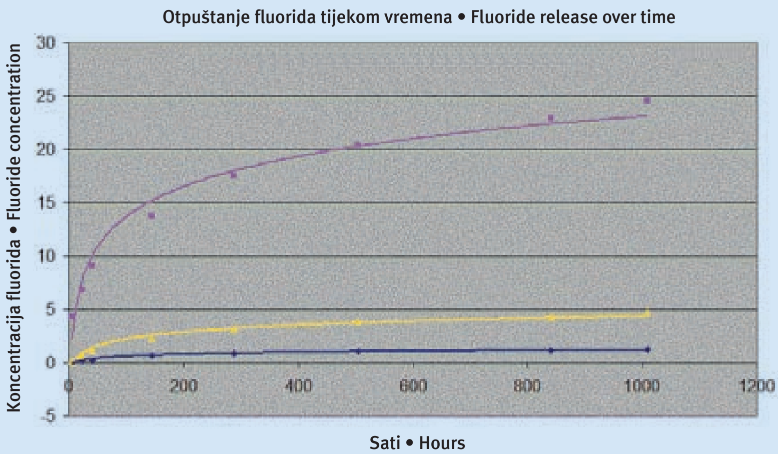
(Sample A: $y=0.2556Ln(x)-0.5713$; sample B: $y=4.0737Ln(x)-5.0637$; sample C: $y=0.9183Ln(x)-1.9826$)

Mean, standard deviation and cumulative fluoride releasing over time were calculated and shown in Table 2.

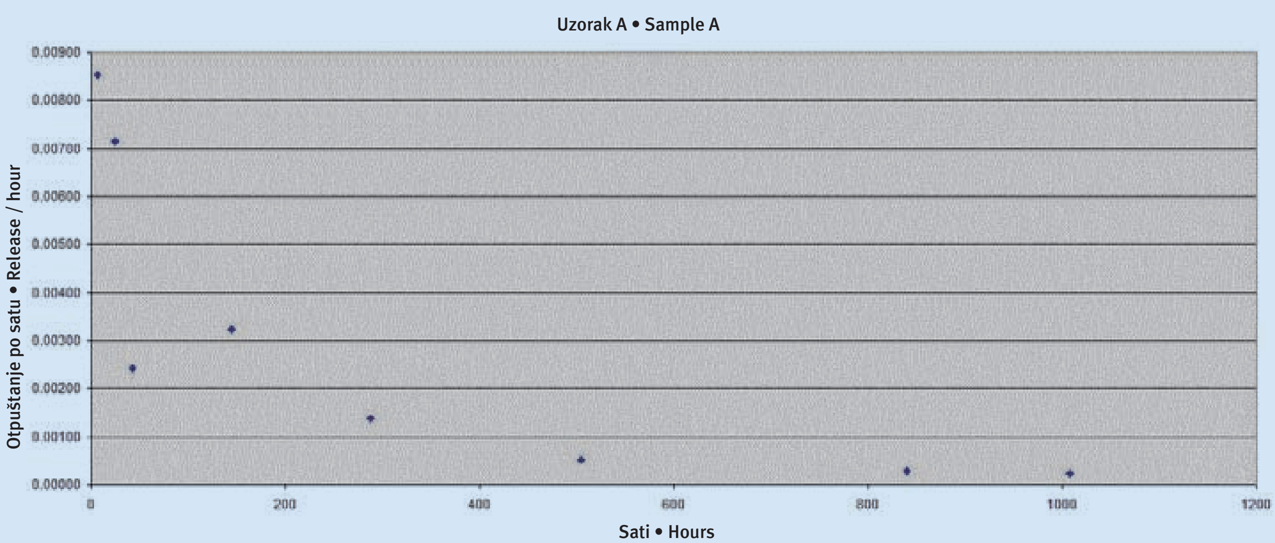
In 10 weeks of testing, sample A released 1.294 mgF^-/L in total. The greatest number of fluoride ions was released during the first 200 hours. The dynamic of fluoride ions release from sample A is shown in Figure 2. At the beginning of the testing, the dynamic of fluoride ions release was significantly greater than in later time periods. During the first 6 hours of testing, the greatest number of released fluoride

Tablica 2. Srednja vrijednost i standardna devijacija uzoraka
Table 2 Mean values and standard deviations of samples

Vremenski interval • Time interval	Skupina A • Sample A		Skupina B • Sample B		Skupina C • Sample C	
	Srednja vrijednost • Mean	Standardna devijacija • Standard deviation	Srednja vrijednost • Mean	Standardna devijacija • Standard deviation	Srednja vrijednost • Mean	Standardna devijacija • Standard deviation
6 sati • hours	0.059	0.018	4.313	1.237	0.199	0.050
24 sati • hours	0.177	0.094	2.538	0.385	0.574	0.323
48 sati • hours	0.073	0.045	2.221	0.387	0.558	0.161
1 tjedan • week	0.542	0.412	4.677	0.467	1.183	0.332
2 tjedna • weeks	0.289	0.220	3.710	0.378	0.987	0.291
4 tjedna • weeks	0.189	0.186	2.903	0.313	0.654	0.275
7 tjedana • weeks	0.216	0.322	2.548	0.294	0.499	0.182
10 tjedana • weeks	0.176	0.164	1.601	0.259	0.429	0.132



Slika 1. Otpuštanje fluoridnih iona (mg/L) tijekom vremena – usporedba uzoraka A, B i C
Figure 1 Release of fluoride ions (mg/L) over time – comparison of samples A, B and C



Slika 2. Dinamika otpuštanja fluoridnih iona (mg/L) u uzorku A – po satima
Figure 2 Dynamics of fluoride ions (mg/L) in sample A - according to hours

U uzorku B bilo je tijekom 10 tjedana izlučeno ukupno 24,512 mgF⁻/L. Na početku je otpuštanje fluoridnih iona bilo značajno i u ispitivanom vremenu postignute su visoke vrijednosti otpuštenih fluoridnih iona (6,851 mgF⁻ /L), a nakon 24 sata dinamika otpuštanja počela se smanjivati. To pokazuje znatno izražen tzv. *burst*-učinak ovog materijala. U prvih šest sati zabilježena je visoka dinamika otpuštanja fluorida od čak 0,718 mgF⁻/L/sat, a nakon desetog tjedna brzina otpuštanja iznosila je samo 0,003 mgF⁻/L/sat (slika 3.).

Uzorak C je ukupno u 10 tjedana otpustio 4,685 mgF⁻/L. Najveća količina fluoridnih iona otpuštena je u prvih 48 sati i s vremenom se znatno smanjila, što upućuje na to da postoji tzv. *burst*-učinak. Dinamika otpuštanja fluoridnih iona iz uzorka C nalazi se na slici 4.

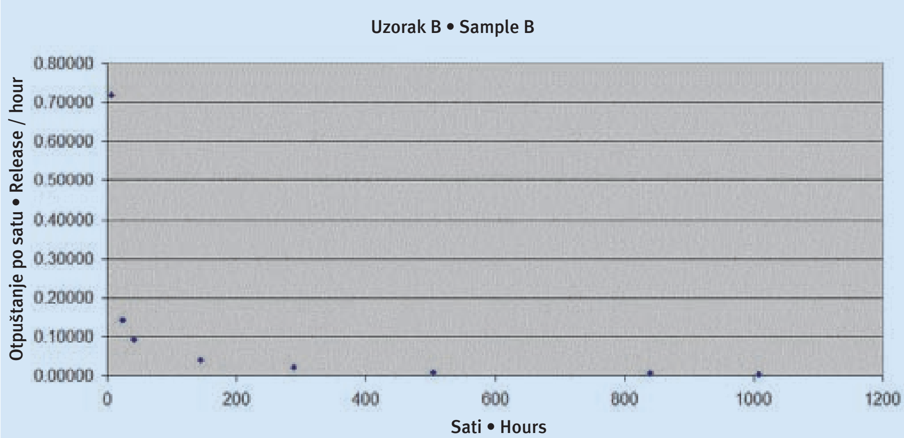
Prosječne vrijednosti i standardne devijacije za sve testirane materijale u ispitivanim intervalima prikazane su u tablici 2.

ions per hour occurred, as much as 0.009 mgF⁻/L. After the first week, the dynamic of fluoride ions release significantly decreased and after 4 weeks the ion release was almost negligible.

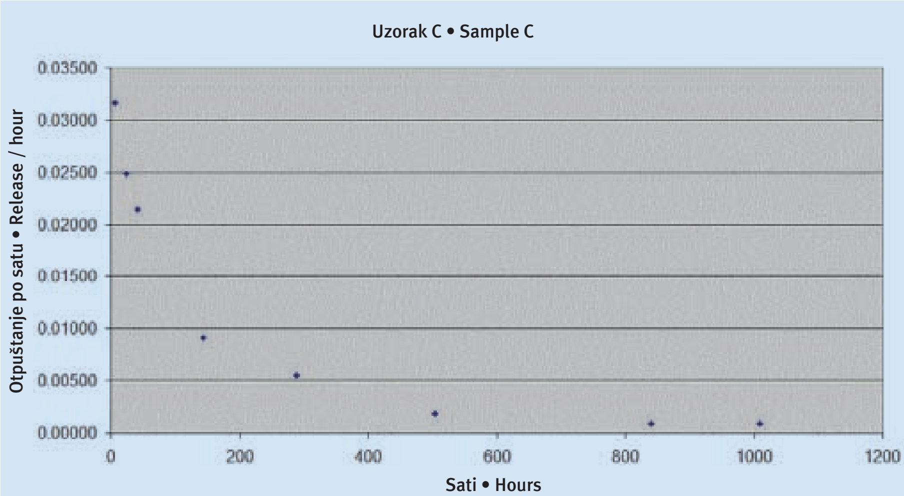
From sample B, 24.512 mgF⁻/L was released in total during 10 weeks. In the beginning, the release of fluoride ions was significant and high values of released fluoride ions (6.851 mgF⁻ /L) were obtained during the measuring whereas, after 24 hours, the dynamics of fluoride ions release in sample B decreased. This fact points to a highly pronounced burst effect of this material. In the first 6 hours, high dynamics of fluoride release was recorded, as high as 0.718 mgF⁻/L/hour, whereas after the 10th week, the speed of release amounted to only 0.00318 mgF⁻/L/hour (Figure 3).

Sample C released 4.685 mgF⁻/L in total in 10 weeks. The greatest quantity of fluoride ions in sample C was released during the first 48 hours and it significantly decreased with time, which points to the existence of the burst effect. The dynamics of fluoride ions release from sample C is shown in Figure 4.

Mean values and standard deviations of fluoride release for investigated time intervals for all tested materials are shown in Table 2.



Slika 3. Dinamika otpuštanja fluorida (mg/L) u uzorku B – po satima
Figure 3 Dynamics of fluoride release (mg/L) in sample B – according to hours



Slika 4. Dinamika otpuštanja fluoridnih iona (mg/L) u uzorku C – po satima
Figure 4 Dynamics of fluoride ions release (mg/L) in sample C – according to hours

Rasprava

Istraživanje i razvijanje materijala u restaurativnoj dentalnoj medicini koji se primjenjuju u terapijske svrhe, a djeluju i preventivno, jako je važno jer objedinjuju cilj i zadatke struke, a to je poboljšati zdravstveno stanje usne šupljine.

Noviji epidemiološki podaci pokazuju da je karijes još uvijek javnozdravstveni problem u mnogim zemljama u razvoju u kojima je zabilježen porast incidencije i kod školske djece i kod odraslih (6). Među čimbenicima koji pridonose porastu karijesa jest i nedostatna izloženost fluoridima (6,7). Korištenje materijala koji otpuštaju fluoride pri izradi trajnih restauracija omogućilo bi potrebnu izloženost fluoridima. Njihova povišena koncentracija postiže se ne samo u području neposrednog kontakta s materijalom za ispun, nego i u slini (5).

Većina autora navodi rezultate otpuštanja fluorida iz dentalnih materijala mjerenih u deioniziranoj vodi i umjetnoj slini (4). Zbog mogućnosti usporedbe rezultata u ovom se istraživanju otpuštanje fluorida iz ispitivanih materijala mjerilo upravo u deioniziranoj vodi. Sadržaj fluorida u restaurativnim materijalima trebao bi biti što je moguće viši, a da pritom nema negativnog učinka na fizikalna ili mehanička svojstva materijala i/ili degradacije ispuna (9). Početno veliko otpuštanje fluorida tzv. *burst* ili intenzivni učinak poželjan je jer će smanjiti djelovanje bakterija koje su možda ostale u unutrašnjosti demineraliziranog dentina te potaknuti caklinu/dentin na remineralizaciju (9). Znatno sniženje otpuštenih fluoridnih iona tijekom sljedećih dana vjerojatno se događa zato što su se pri početnom naglom otpuštanju iona oslobodile velike količine fluoridnih iona pri otapanju čestica stakla u poliakrilnoj kiselini i stvrdnjavanja materijala. Visoke koncentracije fluoridnih iona oslobođene prvog dana mogu uzrokovati i početni učinak površinskog ispiranja. Stalno otpuštanje fluoridnih iona sljedećih se dana pojavljuje zbog mogućnosti fluoridnih iona da difundiraju kroz pore cementa i napukline (10).

Can Karabulut i suradnici proučavali su metode ispitivanja materijala koji otpuštaju fluoride te zaključili da je baš metoda modeliranja linearne regresije, kojom smo se koristili i u ovom istraživanju, najbolja za prikazivanje podataka otpuštanja fluoridnih iona iz dentalnih materijala (7). Iz rezultata dobivenih u ovom istraživanju može se uočiti da uzorci ispitivanih materijala otpuštaju fluoride u logaritamskoj zavisnosti s vremenom. Slične rezultate dobio je i Can Karabulut sa suradnicima u svojem ispitivanju. Oni su se također koristili uzorcima promjera osam milimetara i debljine dva milimetra, ali tijekom šest tjedana (7). Tako provedenim ispitivanjem možemo predvidjeti daljnje ponašanje materijala. Iako, matematički govoreći, materijal nikada neće prestati otpuštati fluoride, ovom se metodom može predvidjeti da će kompozitni materijal *GC Kalore*, prestati otpuštati mjerljive količine fluoridnih iona između četvrtog i sedmog tjedna.

Mousavinasab i Meyers u svojoj su studiji također pokazali da sve vrste staklenih ionomera koje su ispitivali otpuštaju veće količine fluorida u usporedbi s giomerom (*Beautifil, Shofu*) te da kod giomera nema izraženog početnog intenziv-

Discussion

Research and development of materials in restorative dental medicine, which are used for treatment purposes and also have a preventive role, are of great importance because they embrace the goals and aims of the profession in order to improve the condition of the oral cavity.

Recent epidemiological data reveal that caries is still a public health problem in many developing countries in which the increase of caries incidence is recorded in schoolchildren and adults (6). Insufficient exposure to fluorides is among the factors contributing to the increase of caries prevalence (6, 7). The use of materials releasing fluorides during the fabrication of permanent restorations would enable the necessary exposure to fluorides. Not only is the increased concentration of fluorides achieved in the region of indirect contact with filling material, but also in saliva (5).

Most of current authors state the results of fluorides release from dental materials measured in deionized water and artificial saliva (4). For comparison of the results of fluorides release from the tested materials in this study, deionized water was used in particular. Fluoride content in restorative materials should be as high as possible without having adverse effects on either physical or mechanical properties of the material and/or degradation of fillings (9). The initial great release of fluorides, the so-called burst effect, is desirable because it can reduce the possibility of bacterial effects which could have remained within the demineralized dentin and also, it can stimulate the remineralization of enamel/dentin (9). A significant reduction of released fluoride ions is probably caused by the fact that at initial sudden ion burst, a great quantity of fluoride ions was released during the dissolving of glass particles in polyacid and setting of material. Also, high concentrations of fluoride ions released during the first day can be caused by the initial effect of surface moisture contamination. Continuous release of fluoride ions during the next few days occurs due to the ability of fluoride ions to leak into the pores and cracks of the cement (10).

Can-Karabulut et al. studied the methods of testing materials which release fluorides reaching the conclusion that the method of linear regression modeling, which has been used in this study, was the best to present data about the process of fluoride ions release from dental materials (7). From the obtained results in this study, it can be concluded that samples of the tested materials release fluorides in a logarithmic time dependence. Similar results were obtained by Can-Karabulut et al. who in their study also used samples of 8 mm in diameter and 2 mm in thickness but during 6 weeks (7). By testing in this way, further predictions can be made about the behavior of materials. Although, mathematically speaking, materials will never cease to release fluorides; this method can predict that Kalore GC composite material ceases to release measurable quantities of fluoride ions in the period between the 4th and the 7th week.

In their study, Mousavinasab and Meyers also showed that all kinds of the tested glass ionomers released greater quantities of fluorides compared with giomer (Beautifil, Shofu) and that there is no initial pronounced burst effect in the nog (*burst)* učinka koji je kod staklenih ionomernih cemenata vrlo izražen (10).

U ovom se ispitivanju pokazalo da se giomer *Shofu Beautifil II*, prema svojstvima otpuštanja fluorida, ponaša između kompozitnog materijala i staklenog ionomernog cementa. *GC Kalore* nema veliko početno otpuštanje fluoridnih iona jer je stvrdnjavanje materijala odmah završilo svjetlosnom polimerizacijom, već pri izradi preparata za ispitivanje. *GC Equia*, kao stakleni ionomerni cement, stvrdnjava se kemijski. Znači da taj proces neko vrijeme traje. To je razlog za nastanak tzv. *burst* ili intenzivnog učinka kod staklenih ionomernih cemenata.

Karantakis i suradnici u svojem su istraživanju izmjerili najviše otpuštene vrijednosti iona F^- u prva četiri sata nakon miješanja materijala, a postižu vrijednosti od 1,6 do 1,8 μg/mm², što je potvrđeno i u ovom istraživanju (11). U prvih 48 sati praćenja *GC Equia* otpustio je 9,072 mgF^-/L, od ukupno 24,512 mg F^- /L u deset tjedana ispitivanja. Ta vrlo visoka dinamika otpuštanja fluorida od 0,718 mgF^-/L/sat u prvih 6 sati, već nakon 48 sati pada na 0,093 mgF^- /L/satu.

Slične rezultate dobili su Basso i njegovi kolege kada su proučavali otpuštanje fluorida u restorativnim staklenim ionomernim cementima, te su ustanovili visoke vrijednosti tijekom prvog dana, ali koje naglo padaju drugog i trećeg dana ispitivanja (12). Bell i suradnici također su izmjerili koncentraciju od 1 ppm otpuštenih fluorida iz staklenih ionomernih uzoraka debljine 1,5 milimetara i promjera šest milimetara u umjetnoj slini tijekom deset minuta, a kumulativne vrijednosti ukupno otpuštenih fluorida u 24 sata iznosile su otprilike 15 ppm (13). *In vitro* je često potvrđeno da su najviše vrijednosti otpuštenih fluorida u prvih 24 do 48 sati od 5 do 155 ppm za različite vrste staklenih ionomernih cementa (14 – 18). Ispitivanja su pokazala da je kumulativno otpuštanje iona fluora iz staklenih ionomernih cementa kontrolirano difuzijom i slijedi silazni gradijent koji je linearno ovisan o korijenu vremena (19 – 21). Zato se visoke početne vrijednosti fluorida naglo smanjuju nakon 24 do72 sata (12,22,23) i podižu se do približno konstantne vrijednosti između 10 i 20 dana (15,23), što se primjećuje i u *GC Equiae*, staklenom ionomernom materijalu testiranom u ovom istraživanju.

U mnogobrojnim istraživanjima koja su se bavila otpuštanjem fluorida iz kompozitnih materijala zaključeno je da su vrijednosti otpuštenih fluorida mnogo niže od vrijednosti drugih materijala koji otpuštaju fluoride, a rabe se kao restaurativni materijali (12,19,24). To je potvrđeno i u ovom istraživanju koje je pokazalo da, bez obzira na tvrdnju da noviji kompozitni materijali otpuštaju veće količine fluorida, još uvijek nisu bolji od staklenog ionomernog cementa ispitivanog u ovom istraživanju. Od ispitivanih materijala *GC Kalore* otpustio je najmanje fluoridnih iona.

Nekoliko ispitivanja različitih kompozitnih materijala pokazalo je visok raspon početnog otpuštanja fluorida u deioniziranu vodu tijekom 24 sata – od 0,04 do 2,7 ppm koje se snižava do 0,02 do 2 ppm za 30 do 60 dana (16,17). Rezultati ovog ispitivanja pokazuju da *GC Kalore* otpušta najviše fluorida u prvih 200 sati, a već nakon četiri tjedna otpuštanje je zanemarivo.

tested giomer unlike the glass ionomer cements wherein this effect is very pronounced (10).

This study showed that giomer, Shofu Beautifil II, according to fluoride release properties, showed both the properties of composite material and glass ionomer cement. GC Kalore does not initially release large quantities of fluoride ions since the setting of material immediately ended by light curing as soon as the testing mixture was prepared. GC Equia, as glass ionomer cement, sets chemically, which means that the setting lasts for a certain time. This is the reason for the burst effect in glass ionomer cements.

In their study, Karantakis et al. measured the highest released values of F^- ions in the first 4 hours after mixing of material, obtaining values up to 1.6-1.8 μg/mm², which was confirmed by this study (11). In the first 48 hours of measuring, GC Equia released 9.072 mgF^-/L out of the total of 24.512mg F^- /L in 10 weeks of testing. This high dynamics of fluoride release amounting to 0.718 mgF^-/L /hour in the first 6 hours, drops to 0.093 mgF^- /L/hour after the first 48 hours.

Similar results were obtained by Basso et al. who studied the fluoride release in restorative glass ionomer cements wherein they found high values in the first day of testing which significantly dropped in the second and third day of testing (12). Also, Bell et al. determined a concentration of fluorides amounting to 1 ppm released from glass ionomer samples of 1.5 mm in thickness and 6 mm in diameter in artificial saliva in the course of 10 minutes, whereas the cumulative values of all released fluorides during 24 hours amounted to approximately 15 ppm (13). Several *in vitro* studies confirmed that the highest values of released fluorides in the first 24 - 48 hours ranged from 5 to 155 ppm for various kinds of glass ionomer cements (15-18). Testing revealed that cumulative release of fluorine ions from glass ionomer cements was controlled by diffusion and followed the dropping gradient which is linearly dependent on the square-root-of-time (19-21). Therefore, the initial high values of fluorides suddenly decrease after 24 -72 hours (12, 22, 23) and rise to an approximately constant value between 10-20 days (15, 23), which was also observed in GC Equiae, the glass ionomer material tested in this research.

Numerous studies dealing with fluoride release from composite materials reached the conclusion that the values of released fluorides were significantly lower than the values of other materials which also release fluorides and are used as restorative materials (12, 19, 24). This was also confirmed by our study which showed that, regardless of the fact that more recent composite materials release greater quantities of fluorides, they still do not match the glass ionomer cement tested in this research. Out of the tested materials, GC Kalore released the smallest amount of fluoride ions.

Several testings of various composite materials revealed a great range of the initial fluoride release into the deionized water over 24 hours amounting to 0.04- 2.7 ppm which drops to 0.02 - 2 ppm over 30-60 days (16,17). The results of this research point out that GC Kalore releases most fluorides in the first 200 hours, and that after 4 weeks, the fluoride release is negligible. Experiments confirmed that compos-

Eksperimentalno se dokazalo da kompozitni materijali s većim količinama fluorida i ion- otpuštajući kompozit (*Ariston*) otpuštaju više fluorida od uobičajenih fluoridiranih kompozita (15,25,26). Uobičajeni kompozitni materijali otpuštaju fluoride u koncentraciji približno proporcionalnoj logaritmu vremena ili $t_{1/2}$ (26,27,28), a eksperimentalni kompozitni materijali s velikim udjelom fluorida pokazuju linearno otpuštanje proporcionalno vremenu (25,26). Pretpostavlja se da su kod ovih posljednjih visoke vrijednosti otpuštenih fluorida rezultat njihove velike koncentracije u obliku F-Al-silikata i YbF_3 u kombinaciji s visokom topljivošću punila u vodi, velikim prihvaćanjem vode i vrlo difuznom polimernom matricom (16,19,25).

Itota i suradnici istaknuli su da je količina ukupnog i slobodnog fluorida otpuštenog iz giomera veća nego kod kompozita i kompomera, te su zaključili da je staklena ionomerna matrica vrlo važna za otpuštanje fluorida i mogućnost ponovnog punjenja materijala (29). Također su zaključili da giomeri i kompomeri na početku ne otpuštaju intenzivno fluoride (tzv. *burst*-učinak), što je inače svojstveno staklenim ionomernim cementima. U ovom ispitivanju pronađeno je i da giomeri nemaju tako jako izraženo početno otpuštanje fluorida poput staklenog ionomera, no *Shofu Beautifil* otpušta ih znatno više od *GC Kalore*. Najveća količina fluorida ipak je otpuštena u otopinu u prvih 48 sati, a poslije znatno manje. Tako se može zaključiti da određeni, manje istaknuti *burst*-učinak ipak postoji.

No obzirom na to da se u literaturi mogu naći različiti načini ispitivanja otpuštanja fluoridnih iona iz dentalnih materijala – što je razlog velike raspršenosti u prikazivanju i obrađivanju rezultata – teži se boljoj standardizaciji uzorkovanja dentalnih materijala. Korištenje standardnih otopina i odgovarajućih statističkih metoda za obrađivanje podataka sigurno bi pomoglo da se mogu bolje uspoređivati i tumačiti rezultati dobiveni u istraživanjima *in vitro,* što bi olakšalo odabir materijala za izradu ispuna.

Zaključak

Na temelju rezultata ovog istraživanja može se zaključiti da – ako je pri estetski zahtjevnom restaurativnom postupku važno preventivno djelovanje u obliku otpuštanja fluorida – tada giomeri mogu biti materijal izbora.

Sukob interesa

Autori ističu da nisu bili ni u kakvom sukobu interesa.

ite materials with greater quantities of fluorides and ion-releasing composite (Ariston) release more fluorides than the commonly fluoridated composites (15, 25, 26). The common composite materials release fluorides with a concentration which is approximately proportionate to the time logarithm or $t_{1/2}$ (26, 27, 28), whereas experimental composites with a greater share of fluorides reveal a linear fluoride release which is proportionate with time (25, 26). It is assumed that the measured high values of released fluorides in the latter composites are the result of high concentrations of fluorides in the F-Al-silicate and YbF_3 forms in combination with high solubility of sealers in water, great acceptance of water and very diffuse polymer matrix (16, 19, 25).

Itota et al. showed that the quantity of the total and free fluoride released from giomer is greater than in composites and compomers and concluded that the present glass ionomer matrix plays an important role in release of fluorides and also in the possibility of material refilling (29). Also, they concluded that giomers and compomers do not have a great initial release of fluorides in form of burst effect, which is typical of glass ionomer cements. In this study, it was also found that giomers do not have such a pronounced initial release of fluorides such as glass ionomers; however, Shofu Beautifil releases significantly more fluorides than GC Kalore. Yet, the greatest quantity of fluorides was released in the first 48 hours whereas later there were a significantly smaller number of fluorides in the solution. Therefore, it can be concluded that a certain, less obvious burst effect is present.

However, since in literature there are various methods described by which the authors carried out their testing of fluoride ions from dental materials, which is why the results are processed and presented in a scattered way in literature, there is a desire for a better standardization of dental material sampling. The use of standardized solutions and appropriate statistical methods for data processing would certainly result in better comparability and understanding of results obtained by *in vitro* studies which would eventually aid in selecting the right filling material.

Conclusion

Based on the results of this study, it can be concluded that in case of an esthetically demanding restorative procedure, preventive measures in the form of fluoride release are important, and giomers can then be materials of choice.

Conlict of interest

The authors deny any conflicts of interest.

Abstract

Aim: The aim of this *in vitro* study was to determine and to compare the level and dynamics of fluoride release in three types of current filling materials. **Materials and methods:** luoride release was measured in GC Kalore composite, glass ionomer GC Equia cement and Shofu Beautiful II giomer. 20 discs were made from each material (8 mm diameter, 2 mm thickness). Measurements were made during 10 weeks by an ion-selective electrode (ORION EA 940). The linear regression method was used in statistical data processing. **Results:** The GC Kalore composite released 1.29 ppm F^- in 10 weeks of testing. Fluoride release decreased and after 4 weeks of testing, it became impossible to measure by ion-selective electrode. Glass ionomer cement, GC Equia released the greatest number of fluoride ions (24.512 ppm F^-) and the greatest number of fluorides was released during the first 24 hours (6.8507 mgF^-/L). Giomer Shofu Beautiful II released 4.685 ppm F^-. **Conclusion:** The examined giomer released more fluorides than the composite material and therefore, it can be recommended as a material of choice for esthetic fillings in which the caries preventive effect is also important.

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Key words
Composite Resins; Glass Ionomer Cement; Fluorides; giomer

References

1. Linčir I i sur. Farmakologija za stomatologe. 3rd ed. Zagreb: Medicinska naklada; 2011.
2. Marya CM, Ashokkumar BR, Dahiya V, Gupta A. Prevalence and severity of dental fluorosis in endemic fluoride areas of Haryana, India: an epidemiologic study. Acta Stomatol Croat. 2010;44(3):152-8.
3. Ambarkova V, Goršeta K, Glavina D, Škrinjarić I. The effect of fluoridated dentifrice formulations on enamel remineralisation and microhardness after in vitro demineralization. Acta Stomatol Croat. 2011;45(3):159-65.
4. Garcez RM, Buzalaf MA, de Araújo PA. Fluoride release of six restorative materials in water and pH-cycling solutions. J Appl Oral Sci. 2007 Oct;15(5):406-11.
5. Wiegand A, Buchalla W, Attin T. Review on fluoride-releasing restorative materials-fluoride release and uptake characteristics, antibacterial activity and influence on caries formation. Dent Mater. 2007 Mar;23(3):343-62.
6. Mužinić D, Vrček D, Ivanišević Malčić A, Matijević J, Rošin Grget K, Jukić Krmek S. The Concentration of Fluorides in tap Water and Commercial Bottled Beverages. Acta Stomatol Croat. 2012;46(1):23-30.
7. Can-Karabulut DC, Batmaz I, Solak H, Taştekin M. Linear regression modeling to compare fluoride release profiles of various restorative materials. Dent Mater. 2007 Sep;23(9):1057-65.
8. [Database on the Internet]. Wolframalpha. [about 1 p.]. Available from: http://www.wolframalpha.com/
9. Jones S, Burt BA, Petersen PE, Lennon MA. The effective use of fluorides in public health. Bull World Health Organ. 2005 Sep;83(9):670-6.
10. Mousavinasab SM, Meyers I. Fluoride release by glass ionomer cements, compomer and giomer. Dent Res J (Isfahan). 2009 Fall;6(2):75-81.
11. Karantakis P, Helvatjoglou-Antoniades M, Theodoridou-Pahini S, Papadogiannis Y. Fluoride release from three glass ionomers, a compomer, and a composite resin in water, artificial saliva, and lactic acid. Oper Dent. 2000 Jan-Feb;25(1):20-5.
12. Basso GR, Della Bona A, Gobbi DL, Cecchetti D. Fluoride release from restorative materials. Braz Dent J. 2011;22(5):355-8.
13. Bell A, Creanor SL, Foye RH, Saunders WP. The effect of saliva on fluoride release by a glass-ionomer filling material. J Oral Rehabil. 1999 May;26(5):407-12.
14. Freedman R, Diefenderfer KE. Effects of daily fluoride exposures on fluoride release by glass ionomer-based restoratives. Oper Dent. 2003 Mar-Apr;28(2):178-85.
15. Forsten L. Fluoride release and uptake by glass-ionomers and related materials and its clinical effect. Biomaterials. 1998 Mar;19(6):503-8.
16. Hörsted-Bindslev P, Larsen MJ. Release of fluoride from conventional and metal-reinforced glass-ionomer cements. Scand J Dent Res. 1990 Oct;98(5):451-5.
17. Attar N, Turgut MD. Fluoride release and uptake capacities of fluoride-releasing restorative materials. Oper Dent. 2003 Jul-Aug;28(4):395-402.
18. Yap AU, Tham SY, Zhu LY, Lee HK. Short-term fluoride release from various aesthetic restorative materials. Oper Dent. 2002 May-Jun;27(3):259-65.
19. Creanor SL, Saunders WP, Carruthers LM, Strang R, Foye RH. Effect of extrinsic fluoride concentration on the uptake and release of fluoride from two glass ionomer cements. Caries Res. 1995;29(5):424-6.
20. Xu X, Burgess JO. Compressive strength, fluoride release and recharge of fluoride-releasing materials. Biomaterials. 2003 Jun;24(14):2451-61.
21. Guida A, Hill RG, Towler MR, Eramo S. Fluoride release from model glass ionomer cements. J Mater Sci Mater Med. 2002 Jul;13(7):645-9.
22. Mitra SB. In vitro fluoride release from a light-cured glass-ionomer liner/base. J Dent Res. 1991 Jan;70(1):75-8.
23. Dionysopoulos P, Kotsanos N, Pataridou A. Fluoride release and uptake by four new fluoride releasing restorative materials. J Oral Rehabil. 2003 Sep;30(9):866-72.
24. DeSchepper EJ, Berr EA 3rd, Cailleteau JG, Tate WH. A comparative study of fluoride release from glass-ionomer cements. Quintessence Int. 1991 Mar;22(3):215-9.
25. Preston AJ, Agalamanyi EA, Higham SM, Mair LH. The recharge of esthetic dental restorative materials with fluoride in vitro-two years' results. Dent Mater. 2003 Jan;19(1):32-7.
26. Dijkman GE, de Vries J, Lodding A, Arends J. Long-term fluoride release of visible light-activated composites in vitro: a correlation with in situ demineralisation data. Caries Res. 1993;27(2):117-23.
27. Buchalla W, Attin T, Kalb K, Hellwig E. Fluoride release and uptake of a new experimental composite in vitro and in situ. Dtsch Zahnärztl Z. 1998;53:707–12.
28. Cooley RL, Sandoval VA, Barnwell SE. Fluoride release and color stability of a fluoride-containing composite resin. Quintessence Int. 1988 Dec;19(12):899-904.
29. Itota T, Carrick TE, Yoshiyama M, McCabe JF. Fluoride release and recharge in giomer, compomer and resin composite. Dent Mater. 2004 Nov;20(9):789-95.