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IZVORNI ZNANSTVENI RAD
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Valentina Brzović Rajić[1], Ivana Miletić[1], Sevil Gurgan[2], Kristina Peroš[3], Željko Verzak[4], Ana Ivanišević Malčić[1]

Otpuštanje fluora iz staklenog ionomera tretiranog s dva različita premaza

Fluoride Release from Glass Ionomer with Nano Filled Coat and Varnish

[1] Zavod za endodonciju i restaurativnu stomatologiju Stomatološkog fakulteta Sveučilišta u Zagrebu, Hrvatska
Department of Endodontics and Restorative Dentistry, School of Dental Medicine, University of Zagreb, Croatia
[2] Stomatološki fakultet Sveučilišta Hacettepe, Ankara, Turska
School of Dental Medicine, Hacettepe University, Ankara, Turkey
[3] Katedra za farmakologiju Stomatološkog fakulteta Sveučilišta u Zagrebu, Hrvatska
Department of Pharmacology, School of Dental Medicine, University of Zagreb, Croatia
[4] Zavod za dječju I preventivnu stomatologiju Stomatološkog fakulteta Sveučilišta u Zagrebu, Hrvatska
Department of Pediatric and Preventive Dentistry, School of Dental Medicine, University of Zagreb, Croatia

Sažetak

Svrha rada: Ovo istraživanje *in vitro* uspoređuje otpuštanje fluora iz mikrolaminiranog staklenog ionomera temeljenog na stakleno-hibridnoj tehnologiji premazanog dvama različitim premazima. **Materijali i postupci:** Ukupno 18 uzoraka podijeljeno je u skupine po šest uzoraka: (1) stakleni ionomer Equia Forte Fil premazan Equia Forte Coatom (Equia + EC), (2) stakleni ionomer Equia Forte Fil premazan GC Fuji Varnishem (Equia + VC) i (3) nepremazani stakleni ionomer Equia Forte (EQUIA kont). Otpuštanje fluora mjereno je fluor-selektivnom elektrodom (ORION EA 940) nakon 24 sata, 4 dana, 30 dana i 64 dana. ANOVA, Tukeyjev test multiplih usporedbi i paired t-test korišteni su u testiranju razlika među skupinama. **Rezultati:** Statistički značajne bile su razlike među skupinama i četirima točkama u vremenu (ANOVA, $p < 0,0001$). Kumulativno otpuštanje iona fluora nakon 64 dana bilo je redom 66,01 mg/l, 123,54 mg/l i 203,22 mg/l za EQUIA + EC, EQUIA + VC i EQUIA kont. Sve su razlike bile statistički značajno različite, osim one između EQUIA + VC i EQUIA kont. nakon 24 sata. **Zaključci:** Količina otpuštenog fluora bila je značajno manja u uzorcima premazanima nanopunjenim premazom u usporedbi s onima premazanima varnishem i bez premaza.

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Adresa za dopisivanje
Valentina Brzović Rajić
Sveučilište u Zagrebu
Stomatološki fakultet
Zavod za endodonciju I restaurativnu stomatologiju
Gundulićeva 5, 10000 Zagreb, Croatia
tel. 4802 126
faks: +385 1 4802 159
vbrzovic.rajic@sfzg.hr

Ključne riječi
stomatološki materijali; fluoridi; staklenoionomerni cementi; nanočestice; lak

Uvod

Fluor je važno terapijsko i preventivno sredstvo u prevenciji zubnog karijesa i remineralizaciji djelomično demineraliziranih zubnih tkiva kada se topikalno primjenjuje u usnoj šupljini (1). Nekoliko je mehanizama protukarijesnog djelovanja fluora, uključujući inhibiciju bakterijskog metabolizma i rasta, usporavanje demineralizacije i poticanje remineralizacije (2). Zato se otpuštanje fluora smatra važnim svojstvom restaurativnih dentalnih materijala, a pokazalo se da na njegovu razinu otpuštanja utječu sastav materijala, uvjeti pohrane i način stvrdnjavanja (2).

Stakleni ionomeri često se upotrebljavaju u suvremenoj dentalnoj medicini (3). Njihove prednosti pred ostalim restaurativnim materijalima, poput kemijske adhezije, biokompatibilnosti, protektivnog i remineralizirajućeg djelovanja na zubna tkiva, dobro su dokumentirane (4, 5). Tradicionalni SIC-ovi imaju nedostatna fizikalna svojstva te su svrstani u

Introduction

Fluoride is an important therapeutic and preventive agent in dental caries prevention and remineralization of partly demineralized dental tissues, when topically administered in the oral cavity (1). There are several mechanisms of anticariogenic fluoride action including inhibition of bacterial growth and metabolism, hindering demineralization and promoting remineralization (2). Fluoride release is, therefore, considered to be a valuable property of restorative dental materials, and was shown to be influenced by several factors. The material composition, storage conditions and curing method influence the degreee of fluoride release. (2).

Glass ionomer cements are widely used in contemporary dentistry (3). Their advantages over other restorative materials such as chemical adhesion, biocompatibility, protective and remineralizing action on dental tissues are well documented (4,5). Traditional GICs have unfavorable physical properties

privremene materijale neprikladne za trajne ispune (6). Bolja fizikalna svojstva postižu se optimizacijom omjera kiseline i fluoroaluminosilikatnog stakla te veličine i distribucije čestica (4). Novi restaurativni koncept na temelju tehnologije SIC-ova razvijen je 2007., a sastojao se od Fuji IX GP Extra SIC-a i *coata* (svjetlosno polimerizirajućeg premaza) punjenog nanopunilima, te je 2011. godine preimenovan u Equia Fil. Equia Forte (GC, Tokio, Japan) predstavljen 2015. kao novi materijal u sklopu stakleno-hibridne tehnologije. Istaknuto je da sadržava visokoviskozni konvencionalni SIC u kombinaciji s *coatom* punjenim nanopunilima (Equia Forte Coat, GC, Tokio, Japan) (7). Equiin prašak sastoji se od 95 % stroncij-fluoroaluminosilikatnog stakla, uključujući visokoreaktivne male čestice, a 5% čini poliakrilna kiselina. Tekuća komponenta sastoji se od 40 % vodene otopine poliakrilne kiseline. Stroncij je odgovoran za povećanu radiopaktnost te nema neželjenih učinaka na izgled cementa (8). Ta zamjena kalcija stroncijem povećala je otpuštanje fluora (9). Kako bi se fluor otpustio iz materijala, sol fluorida treba disocirati, a fluor difundirati kroz cement. Budući da je kalcij elektropozitivniji od stroncija, CaF_2 je manje topljiv od SrF_2 (9). Equia Coat sastoji se od 50 % metil-metakrilata i 0,09 % kamforkinona. Taj hidrofilni niskoviskozni površinski premaz brtvi površinu SIC-a, smanjuje abrazivno trošenje i povećava kompresivnu čvrstoću restauracije tijekom prvih mjeseci do postizanja potpune maturacije te poboljšava estetiku tzv. *glaze*-efektom (4, 10, 11). Nadalje, pokazalo se da klinička izvedba novoga restaurativnog sustava zadovoljava (12, 13). Jedno od najvažnijih svojstava materijala temeljenih na SIC-u jest njihov protukarijesni potencijal. Odgođena demineralizacija susjednih zdravih tkiva i remineralizacija demineraliziranog podležećeg dentina, uvelike su posljedica otpuštanja fluora iz restaurativnog materijala (14, 15).

Svrha ovog istraživanja *in vitro* bila je evaluirati i usporediti otpuštanje fluora iz Equia Forte Fila (GC, Tokio, Japan) premazanog dvama različitim površinskim premazima – Equia Forte Coatom (GC, Tokio, Japan) i zaštitnim premazom Fuji Varnish (GC, Tokio, Japan).

Materijali i postupci

Za izradu uzoraka korišteni su cilindrični aluminijski kalupi (promjera 8 mm i 2 mm visine). Promjer i visina mjereni su digitalnom pomičnom mjerkom. Equia Forte Fil pripremljen je prema uputama proizvođača i apliciran u kalupe. Gornja površina svakog uzorka prekrivena je celuloidnom vrpcom i predmetnim stakalcem na sobnoj temperaturi te je uzorak ostavljen 10 minuta da se stvrdne. Equia Forte Coat apliciran je na šest uzoraka i osvijetljen 20 sekunda, šest uzoraka premazano je Fuji Varnishem koji je ostavljen da se veže bez polimerizacije, a šest uzoraka ostavljeno je bez premaza. Upotrijebljena sredstva za premazivanje nisu sadržavala fluor. Sastojci Equia forte coata su niskoviskozni monomer metil-metakrilat, monomer estera fosforne kiseline i fotoinicijator, a Fuji Varnisha izopropil acetat, aceton, kukuruzno ulje i cinamaldehid. Uzorci su zatim izvađeni iz kalupa primjenom tlaka s jedne strane i pohranjeni 24 sata u vlažnom okolišu

and they have been categorized as temporary materials not suitable for permanent restorations (6). Better physical properties were achieved by optimizing acid-fluoroaluminosilicate glass ratio and particle size and distribution (4). In 2007 a new restorative concept based on GIC technology consisting of Fuji IX GP Extra and nanofilled coat was developed, and it was renamed Equia Fil in 2011. In 2015, Equia Forte (GC, Tokyo, Japan) was launched as a new material based on glass hybrid technology, consisting of a highly viscous conventional GIC combined with a nanofilled coating material (Equia Forte Coat, GC, Tokyo, Japan) (7). Equia's powder consists of 95% strontium fluoroaluminosilicate glass, including the newly added highly reactive small particles, and 5% polyacrylic acid. The liquid component consists of 40% aqueous polyacrylic acid. Strontium is responsible for increased radiopacity and it does not have any undesired effects on the appearance of the cement (8). This substitution of calcium with strontium has enhanced fluoride release (9). For the fluoride to be released, the salt needs to dissociate and diffuse through the bulk cement. Since calcium is more electropositive than strontium, CaF_2 is less soluble than SrF_2 (9). Equia Coat consists of 50% methyl methacrylate and 0.09% camphorquinone. This hydrophilic low viscosity nanofilled surface coating seals the GIC surface, reduces abrasive wear and the fracture strength of the restoration during the first months until complete maturation is achieved. Besides it improves esthetics by glaze effect (4,10,11). Furthermore, it was shown that the clinical performance of the newly developed restorative system is quite satisfying (12,13). One of the most important properties of GIC-based materials is their anticariogenic potential. Delayed demineralization of adjacent sound tissues and remineralization of demineralized underlying dentin are largely the result of fluoride release from the restorative material (14,15).

The aim of this *in vitro* study was to evaluate and compare the fluoride release from Equia Forte Fil (GC, Tokyo, Japan), coated with two different surface coating agents Equia Forte Coat (GC, Tokyo, Japan) and Fuji Varnish protective coating (GC, Tokyo, Japan).

Materials and methods

Cylindrical aluminum molds (8 mm diameter and 2 mm depth) were used to prepare the samples. The diameter and depth were measured using an electronic digital caliper. Equia Forte Fil was prepared according to the manufacturer's instructions and packed into the molds. The top surface of each specimen was covered with a celluloid strip and a glass slide at room temperature and the specimen was allowed to set at room temperature for 10 min. Equia Forte Coat was applied on six samples and light-cured for 20 s, six samples were coated with Fuji Varnish which was left to self-cure and six were left uncoated. Both agents were free of fluoride. Equia forte coat content includes low viscosity monomer methyl methacrylate, phosphoric acid ester monomer and photoinitiator, whereas Fuji Varnish contains isopropyl acetate, acetone, cornmint oil and cinnamaldehyde. The specimens were subsequently removed from the molds by ap-

na 37 °C. Svaki uzorak uronjen je u 5 ml deionizirane vode u polietilenskim posudama i inkubiran 24 sata na 37 °C. Nakon 24 sata uzorci su izvađeni iz posuda te je izmjerena koncentracija fluorida u destiliranoj vodi fluor-selektivnom elektrodom tipa 96 – 09 (Boston, Mass, SAD) i mikroprocesorom ORION EA 940 (Orion Res Inc, SAD). Prije mjerenja koncentracije fluora, prema uputama proizvođača provjerena je točnost mjernog instrumenta i inklinacija elektrode te je svakom uzorku dodano 0,5 ml TISAB-a III (Total Ionic Strength Adjustment Buffer; Merck KGaA, Darmstadt, Njemačka) kako bi se postigla konstantna ionska snaga i pH.

Nakon toga uzorci su isprani, osušeni, izvagani te ponovno uronjeni u novu posudu s 5 ml deionizirane vode. Mijenjanje destilirane vode i mjerenje sadržaja fluorida u njoj učinjeni su nakon 1, 4, 30 i 64 dana u triplikatima za svaki uzorak, a vrijednosti koncentracije izražene su u mgF/L (ppm F^-).

Podatci su obrađeni statističkim paketom SAS. ANOVA je korištena za usporedbu srednjih vrijednosti, Tukeyjev test za multiple usporedbe te paired t-test s Bonferronijevom korekcijom za usporedbu srednjih vrijednosti u različitim točkama vremena. Razina značajnosti za sve testove bila je $p < 0,05$.

Uzorci koji nisu korišteni za određivanje razine otpuštanja fluora, analizirani su s pomoću SEM-a. Uzorci su stavljeni u polimernu masu koja provodi struju, obrađeni brusnim papirom (P320, P500, P1000, P2400, P4000) na 300 rpm uz vodeno hlađenje, ispolirani na 150 rpm i primijenjenom silom od 30 N s pomoću dijamantnih pasta (3µm i 1 µm) i lubrikanta.

Rezultati

Rezultati otpuštanja iona fluora nalaze se u tablici 1. Otpuštanje fluora značajno se razlikovalo među skupinama ($p < 0,0001$) i u različitim točkama vremena (ANOVA, $p < 0,0001$). Najmanje otpuštenih iona fluora zabilježeno je u skupini EQUIA + EC, zatim u skupini EQUIA + VC, a najveće otpuštanje fluora bilo je u skupini s nepremazanim uzorcima. Tukeyjev test pokazao je da je bilo slično otpuštanje fluora nakon 24 sata iz uzoraka EQUIA + VC i EQUIA kont. Nakon 64 dana zabilježena je značajna razlika u otpuštanju fluora između skupina EQUIA + EC i EQUIA kont. Rezultate kumulativnog otpuštanja iona fluora vidi u tablici 2 i na slici 1.

Regresijska analiza pokazala je sljedeće relacije između kumulativnog otpuštanja fluora (y) i vremena (t):

EQUIA + EC	$y = 13,0 \cdot \ln t + 43,5$
EQUIA + VC	$y = 27,6 \cdot \ln t + 75,3$
EQUIA kont.	$y = 66,6 \cdot \ln t + 87,3$

Deskriptivna statistika za mase uzoraka prikazana je u tablici 3.

Razlike među skupinama nisu bile značajne (ANOVA test, $p = 0,15$), ali se masa značajno promijenila tijekom vremena (ANOVA test, $p = 0,0001$). *Post hoc* usporedba pokazala je da su se promjene dogodile u svim uzorcima.

plying pressure at one side and stored in a moist environment at 37°C for 24 h. Each specimen was immersed in 5 ml of deionized water in polyethylene vials and incubated at 37°C for 24 hours. After 24 h, the samples were removed from the vials and the concentration of fluoride ions in the distilled water was measured using a fluoride ion-selective electrode type 96-09 (Boston, Mass, USA) and a microprocessor analyzer ORION EA 940 (Orion Res Inc., USA). Prior to the measurements of the fluoride concentration, the accuracy of the measuring instrument was checked as well as the electrode inclination according to the manufacturer's instructions, and 0.5 ml of TISAB III (Total Ionic Strength Adjustment Buffer; Merck KGaA, Darmstadt, Germany) was added to each sample to achieve constant ionic strength and ph.

Furthermore, the specimens were rinsed, dried, weighted and then reimmersed into a new vial containing 5 ml of deionized water. The changing of distilled water and the fluoride content measurements were performed on days 4, 30 and 64 in triplicate for each sample and expressed in mg/L (ppm F^-).

Data were statistically analysed using SAS statistical package. ANOVA was used for the comparison of means, Tukey's test for multiple comparisons, and paired t-test with Bonferroni correction for the comparison of means at different time points. The significance level for all tests was $p<0.05$.

Other specimes than those used for the fluoride release measurements were analysed using SEM. The specimens were placed into an electrically conductive polymer mass, grinded at 300 rpm under water cooling using sand paper (P320, P500, P1000, P2400, P4000), polished at 150 rpm with 30 N force applied using diamant pastes (3µm and 1 µm) and lubricant.

Results

The results for fluoride ion release are given in Table 1. The fluoride release significantly differed between groups ($p<0.0001$) and at different time points (ANOVA, $p<0.0001$). The least fluoride release was noted in EQUIA+EC group, followed by EQUIA+VC group. The greatest fluoride release was in the group with uncoated samples. The Tukey's test showed that after 24 hours the release of fluoride forms EQUIA+VC and EQUIA cont. samples were similar. After 64 days a significant difference in fluoride release was noted between EQUIA+EC and EQUIA cont. The results of cumulative fluoride ion release are given in Table 2 and shown in Fig. 1.

Regression analysis revealed the following relation between cumulative fluoride release (y) and time (t):

EQUIA+EC	$y = 13.0 \cdot \ln t + 43.5$
EQUIA+VC	$y = 27.6 \cdot \ln t + 75.3$
EQUIA cont	$y = 66.6 \cdot \ln t + 87.3$

Descriptive statistics for sample weights are given in Table 3.

The differences between the groups were not significant (ANOVA test, $p=0.15$), but weight significantly changed over time (ANOVA test, $p=0.0001$). *Post hoc* comparison showed that changes occurred in all samples.

Tablica 1. Otpuštanje iona fluora – mg/l (srednja vrijednost i standardna devijacija – st. d.)
Table 1 Fluoride release in mg/l (Mean and standard deviation, st.d.)

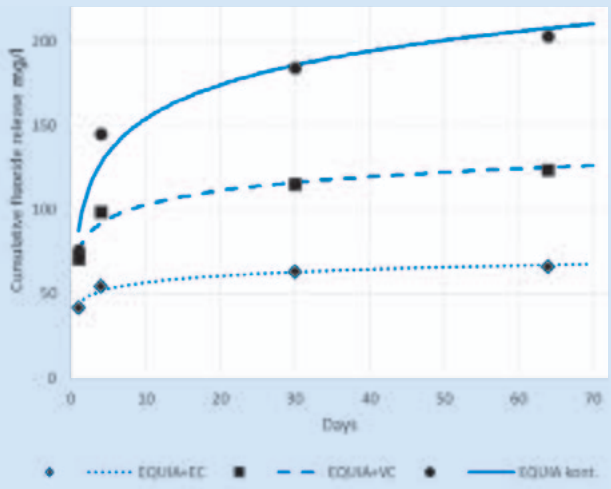
	EQUIA+EC	EQUIA+EC	EQUIA+VC	EQUIA+VC	EQUIA cont	EQUIA cont
	mean	st.d.	mean	st.d	mean	st.d
24h	41.57	(21.3)	70.97	(11.2)	75.95	(17.9)
4 days	12.76	(9.2)	27.61	(14.1)	68.97	(12.6)
30 days	8.60	(4.2)	16.63	(10.5)	39.16	(11.5)
64 days	3.08	(3.4)	8.33	(6.6)	19.15	(14.6)

Tablica 2. Kumulativno otpuštanje iona fluora u mg/l (srednja vrijednost i standardna devijacija – st. d.)
Table 2 Cumulative fluoride ion release in mg/l (Mean and standard deviation, st.d.)

	EQUIA+EC	EQUIA+EC	EQUIA+VC	EQUIA+VC	EQUIA cont	EQUIA cont
	mean	st.d.	mean	st.d	mean	st.d
24h	41.57	(21.3)	70.97	(11.2)	75.95	(17.9)
4 days	54.33	(30.2)	98.58	(24.7)	144.92	(21.4)
30 days	62.93	(33.4)	115.21	(33.7)	184.07	(27.5)
64 days	66.01	(33.6)	123.54	(36.4)	203.22	(34.6)

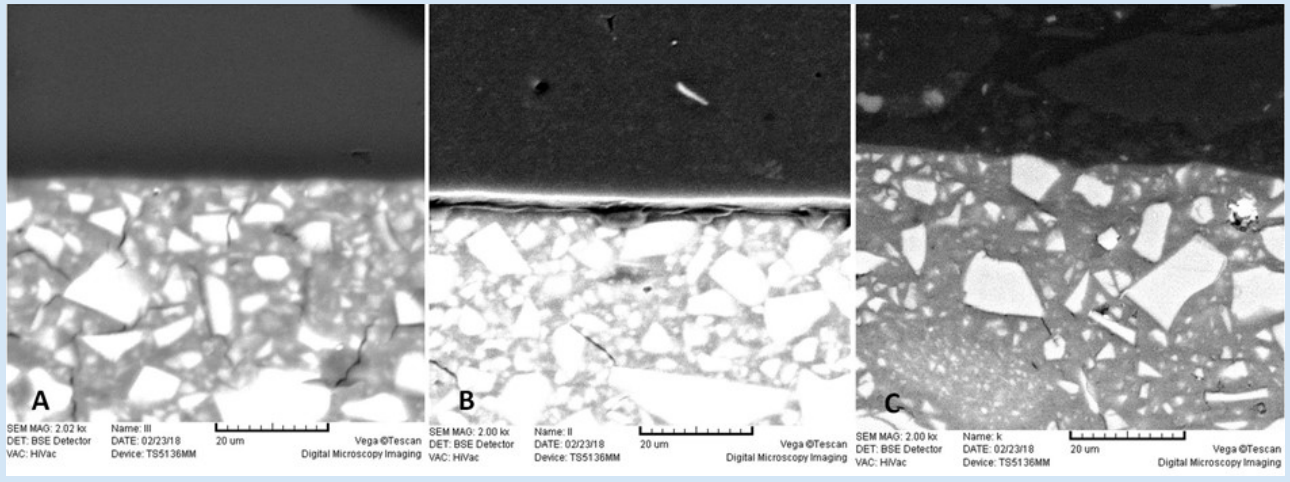
Tablica 3. Mase uzoraka (srednja vrijednost i standardna devijacija – st. d.)
Table 3 Sample weights (Mean and standard deviation, st.d.)

	EQUIA+EC	EQUIA+EC	EQUIA+VC	EQUIA+VC	EQUIA cont	EQUIA cont
	mean	st.d.	mean	st.d	mean	st.d
24h	0.304	(0.04)	0.296	(0.02)	0.269	(0.02)
4 days	0.304	(0.04)	0.302	(0.02)	0.280	(0.02)
30 days	0.298	(0.04)	0.299	(0.02)	0.273	(0.02)
64 days	0.317	(0.04)	0.307	(0.02)	0.276	(0.02)



Slika 1. Otpuštanje fluora tijekom vremena za tri skupine uzoraka – EQUIA + EC, EQUIA+VC i EQUIA kont.
Figure 1 Fluoride release over time for the three groups of samples: EQUIA+EC, EQUIA+VC and EQUIA cont.

Slika 2. Reprezentativni uzorci Equia Forte s (A) Equia Forte Coatom (EQUIA + EC); (B) premazani Fuji Varnishem (EQUIA + VC); i (C) bez sredstava za premazivanje (EQUIA kont); SEM analiza otkrila je da Equia Forte Coat bolje adherira na staklenoionomerni materijal negoli Fuji Varnish
Figure 2 Representative Equia Forte glass hybrid specimens with (A) Equia Forte Coat (EQUIA+EC); (B) covered with Fuji Varnish (EQUIA+VC); and (C) without coating agent (EQUIA cont). SEM analysis revealed that there was better adhesion of Equia Forte Coat than Fuji Varnish onto the underlying GIC material.



SEM analiza pokazala je da Equia Forte Coat bolje prilježe uz stakleni ionomer Equia Forte Fil negoli Fuji Varnish (slika 2.).

Rasprava

U načelu postoje dvije vrste premaza za zaštitu staklenih ionomera nakon postavljanja i početnog stvrdnjavanja, kako bi se spriječila kontaminacija vlagom i gubitak nevezane vode. To su jednostavne otopine polimera u otapalu i svjetlosnopolimerizirajući niskoviskozni monomeri. Pojedina istraživanja pokazuju da svjetlosnopolimerizirajući premazi (*coats*) učinkovitije štite SIC od isušivanja, negoli jednostavni premazi (*varnishes*) te da poboljšavaju njegova fizikalna svojstva (16). U ovom istraživanju korišteni su Equia Forte Coat koji sadržava niskoviskozni monomer metil-metakrilat, monomer estera fosforne kiseline i fotoinicijator te Fuji Varnish koji sadržava izopropil acetat, aceton, kukuruzno ulje i cinamaldehid. Rezultati pokazuju da je značajno više fluora otpušteno iz uzoraka Equia Forte Fil SIC-a premazanih Fuji Varnishem, sugerirajući da Equia Coat bolje brtvi površinu SIC-a. SEM analiza pokazala je da je površina uzoraka bila glatkija kada je bila premazana obama premazima, što može implicirati smanjenu tendenciju pričvršćivanja bakterija na površinu (17). Nadalje, SEM analiza također je pokazala da je adhezija Equia Forte Coata na podležeći SIC bila bolja nego što je to bio slučaj s Fuji Varnishem. To je vjerojatno zbog tehnologije nanopunila na kojoj se temelji Equia Forte Coat, a koja omogućuje jednoličnu disperziju čestica punila (17). Fuji Varnish, pak sadržava molekule polimera otopljene u organskom otapalu. Nakon što se ispun SIC-a premaže *varnishem*, otapalo hlapi i ostavlja molekule kao tanki sloj ili film. Te molekule veće su od nanočestica iz Equia Forte Coata i to vjerojatno utječe na debljinu filma obaju premaza (slika 2.).

Prije je utvrđeno da način stvrdnjivanja – svjetlosnopolimerizirajući ili kemijski – utječe na razinu otpuštanja fluora iz smolom modificiranih SIC-ova i dvostruko polimerizirajućih smolastih cementa. Pokazalo se da polimerizacija inicirana svjetlom povećava gustoću polimerne mreže, što rezultira smanjenim propuštanjem smolastoga matriksa za ione fluora (18, 19). No naši rezultati, koji pokazuju veće otpuštanje fluora u uzorcima premazanima Fuji Varnishem koji nije polimeriziran svjetlom, ne mogu se pripisati povećanoj gustoći veza unutar SIC-a nakon polimerizacije svjetlom pri premazivanju *coatom*, jer je Equia Forte Fil materijal koji se stvrdnjava samo kemijski.

U ovom istraživanju ioni fluora otpuštani su u logaritamskoj vremenskoj ovisnosti u svim trima skupinama uzoraka (slika 1.), slično kao u prijašnjim studijama (20, 21). Kako je već spomenuto, ovaj početni *burst*-efekt poželjan je u smislu protukarijesnog učinka jer potiče remineralizaciju cakline i dentina i djeluje protubakterijski (14, 15, 22, 17). U slučaju uzoraka premazanih Equia Forte Coatom, razdoblje razmjerno konstantnog otpuštanja fluora dosegnuto je nakon četiri dana, slično kao na nepremazanim uzorcima i uzorcima premazanima *varnishem*, ali je početno otpuštanje fluora bilo znatno manje u skupini uzoraka premazanih Equia Forte Coatom. To je u skladu s ostalim istraživanjima u kojima je ot-

The SEM analysis showed that Equia Forte Coat adhered better to Equia Forte Fil glass ionomer than Fuji Varnish (Figure 2).

Discussion

Generally, there are two types of coatings used for the protection of GICs after placement and initial hardening to avoid contamination by moisture and loss of unbound water: simple solutions of polymer in solvent and light-curable low viscosity monomers. There are experiments revealing that light-curable coats protect GICs more effectively from drying out than simple varnish, and that they improve the physical properties of GICs (16). Coating agents used in our study were Equia Forte Coat containing a low viscosity monomer methyl methacrylate, phosphoric acid ester monomer and photoinitiator, and Fuji Varnish containing isopropyl acetate, acetone, cornmint oil and cinnamaldehyde. Our results show that there was significantly more fluoride released from Equia Forte Fil specimens when they were coated with Fuji Varnish indicating that Equia Coat seals the GIC surface more effectively. The SEM analysis of the specimens showed that the surface was smoother when covered with both coating agents, which could imply a reduced tendency of bacteria to adhere to the surface. (17). Furthermore, the SEM analysis also showed that Equia Forte Coat adhered better than Fuji Varnish to the underlying GIC. This is probably due to the nanofiller technology used in Equia Forte Coat enabling uniform dispersion of the filler particles (17). Fuji Varnish on the other hand, contains polymer molecules dissolved in organic solvent. After the GIC filling is covered with varnish, the solvent evaporates, leaving the solute as a thin layer or film. The solute molecules are larger than the nano-particles of the Equia Forte Coat and this probably influences the film thickness of both coatings (Figure 2).

It was previously shown that curing method, either light or chemical curing, influences fluoride release from resin modified glass ionomers and dual-cured resin cements, and it was shown that the photoinitiated polymerization enhances cross-linking density resulting in the reduced resin matrix permeability for fluoride ions (18,19). However, our results of increased fluoride release in the samples coated with Fuji Varnish that was not light cured can hardly be explained with the enhanced cross-linking upon light curing, since Equia Forte Fil is a material that sets by chemical curing alone.

In our study, fluoride was released in a logarithmic time dependence in all three groups (Figure 1), similarly as in previous studies (20, 21). As it was already mentioned, this initial burst effect is desirable in the context of anticariogenic action because it stimulates remineralization of enamel and dentin and has an antibacterial effect (14, 15, 22, 17). In the case of samples coated with Equia Forte Coat, the period of fairly constant fluoride release rate was reached after 4 days, similarly as in uncoated and varnished samples, but the initial fluoride release was significantly smaller in the group coated with Equia Forte Coat. This is in concordance with other studies where 60-76% of reduction in fluoride release from the coated GICs was reported (23, 24). This probably occurred be-

puštanje fluora bilo smanjeno za 60 do 76 % kada su SIC-ovi bili premazani (23, 24). Pretpostavlja se da je to zato što je površinski sloj nematuriranog SIC-a topljiviji i skloniji eroziji ako nije zaštićen premazom (25). Općenito, rezultati ovog istraživanja u skladu su s rezultatima ranijih istraživanja koja pokazuju da je najveće otpuštanje fluora u prvih 24 do 48 sati, a varira od 5 do 155 ppm za različite SIC-ove (26, 27).

Nakon početnog *bursta*, ioni fluora i dalje se otpuštaju jer ne reagiraju kemijski tijekom reakcije stvrdnjivanja te mogu difundirati niz koncentracijski gradijent i biti otpušteni u usnu šupljinu ili preuzeti u stakleni ionomer ako je izložen otopinama s visokom koncentracijom fluora (15, 20). U našem istraživanju je otpuštanje fluora u svim trima skupinama slijedilo isti nagib krivulje jer je bilo određeno sastavom čestica punila i matriksom vezanog materijala – ioni fluora difundiraju kroz pore SIC-a (15). Jednako otpuštanje fluora uočeno je u prijašnjim istraživanjima, u konvencionalnim i smolom modificiranim SIC-ovima (20, 25, 26, 27). Na temelju zabilješki o otpuštanju fluora u ovisnosti o vremenu, može se pretpostaviti dinamika otpuštanja fluora u budućnosti i trenutak u budućnosti kada će otpuštanje fluora prestati. U istraživanju Arbabzadeh-Zavareha i suradnika (28) količina otpuštanog fluora 60. dan mjerenja smatrala se početnom razinom otpuštanja nakon iscrpljivanja materijala. No utvrđeno je da staklenoionomerni materijali mogu vrlo dugo ujednačeno otpuštati fluor (barem 5 godina) (29).

Uočeno je da su uzorci Equia Fortea otpuštali nešto više iona fluora negoli neki drugi SIC-ovi (17). Razlog bi mogao biti u zamjeni kalcijevih iona stroncijevim ionima, što malo povećava razinu otpuštanja fluora jer se SrF_2 bolje otapa u manje kiselom okolišu, negoli CaF_2, što rezultira većim otpuštanjem fluora (9).

Naši rezultati pokazali su da je porast mase bio najveći u uzorcima premazanima *coatom*. To je vjerojatno zbog hidrofilnog monomera u svjetlosnopolimerizirajućem *coatu* čija površina ostaje djelomično nepolimerizirana zbog inhibicije polimerizacije kisikom (30). To može potaknuti apsorpciju vode i pridonijeti povećanju mase.

Pri interpretaciji rezultata ovog istraživanja u kliničkom kontekstu, mora se uzeti u obzir da nisu bili simulirani oralni uvjeti oscilirajućeg pH, temperature i okluzalnog opterećenja. U okviru granica ovog istraživanja može se zaključiti da, u usporedbi s *varnishem* i kontrolnim uzorcima, nanopunjeni *coat* smanjuje otpuštanje fluora iz staklenoionomernih materijala, ali količine se i dalje čine prihvatljivima za karijesnoprotektivno djelovanje, posebno s obzirom na pozitivne učinke premazivanja na mehanička svojstva SIC-a kao mogućeg alternativnog materijala za trajne ispune.

Sukob interesa

Autori nisu bili u sukobu interesa.

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cause the superficial layer of immature GIC is more readily dissolved and eroded if it is not protected (25). Generally, our results are in line with previous studies reporting that the highest values of released fluoride occur in the first 24 - 48 hours ranged from 5 to 155 ppm for different GICs (26,27).

After the initial burst, constant fluoride release occurs because fluoride ions do not react chemically during the setting reaction, and since they remain unreacted they can diffuse down their concentration gradient and are released into the oral environment, or taken up by the glass ionomer if it is exposed to solutions with high fluoride concentration (15,20). In our study, fluoride release after setting continued to follow the same pattern in all three groups because the release is determined by filler particles composition and the matrix of set material: fluoride ions diffuse through the pores of the GIC (15). The same pattern of fluoride release was observed in previous studies, in conventional GICs and modified GICs (20, 25, 26, 27). The recordings and their time dependence enable predictions about the rate of fluoride release in the future, and a point in time when the release would cease. In the study of Arbabzadeh-Zavareh *et al.* (28) the amount of fluoride release measurement on day 60 was considered the base measurement of fluoride release after exhaustion of the materials. However, it was shown that glass ionomer materials are able to release fluoride at a sustained rate for long periods of time (at least 5 years) (29).

It was noted that the Equia Forte samples released somewhat more F^- ions than some other GICs (17). The reason could be a replacement of Ca^{2+} with Sr^{2+} ions which slightly enhances fluoride release rate because SrF_2 is more readily dissociated in less acidic environment than CaF_2 resulting in a higher fluoride release (9).

Our results show that weight increase was the highest in the case of specimens that were coated. This is probably due to the presence of hydrophilic monomer within the light-curable coat which surface remains partly unreacted due to the polymerization inhibition by oxygen (30). This could lead to water sorption contributing to weight increase.

When interpreting the results of this study in clinical context, it must be considered that oral conditions with oscillating pH, temperature and occlusal loading were not simulated.

Within the limits of this study, it can be concluded that the nanofilled coat inhibits the release of fluoride from the GIC material compared to varnish and control samples, but the quantities still seem satisfactory for caries protective action, especially considering beneficial effects of coating on mechanical properties of GIC as a possible alternative material for long-term restorations.

Conflict of Interest

None declared

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Abstract

Objective: This *in vitro* study compares the fluoride release from microlaminated glass ionomer based on glass hybrid technology coated with two different surface coating agents. **Materials and Methods:** A total of 18 samples were divided into three groups of six samples each: (1) glass ionomer Equia Forte Fil coated with Equia Forte Coat (Equia+EC), (2) glass ionomer Equia Forte Fil coated with GC Fuji Varnish (Equia+VC) and (3) uncoated glass ionomer Equia Forte (EQUIA cont). Fluoride release was measured using an ion-selective electrode (ORION EA 940) after 24 hours, 4 days, 30 days and 64 days. Repeated measures ANOVA, multiple comparisons, Tukey's test and paired t-test were used to test the differences between the groups. **Results:** The differences between the groups and four time points were statistically significant (ANOVA, $p<0.0001$). Cumulative fluoride ion release after 64 days was 66.01 mg/l, 123.54mg/l and 203.22 mg/l for EQUIA+EC, EQUIA+VC and EQUIA cont, respectively. All the differences were statistically significant except the difference between EQUIA+VC and EQUIA cont after 24 hours. **Conclusions:** The amount of released fluoride was significantly lower in the samples coated with nanofilled surface coating agent compared to the samples coated with varnish and uncoated samples.

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Address for correspondence
Valentina Brzović Rajić
School of Dental Medicine
University of Zagreb
Gundulićeva 5, 10000 Zagreb, Croatia
Phone: +385 1 4802 126
Fax: +385 1 4802 159
vbrzovic.rajic@sfzg.hr

Key words
Dental Materials; Fluorides; Glass Ionomer Cements; Nanoparticles; Varnish

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