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Antonela Šošić[1], Ivan Šalinović[2]*, Ivana Miletić[2], Salvatore Sauro[3, 4], Ivana Kekez[5], Ana Ivanišević[2]

Microhardness and Chemical Composition of Glass Ionomer and Glass Hybrid Cements Modified with Experimental Bioactive Glasses

Mikrotvrdoća i kemijski sastav staklenoionomernih i staklohibridnih cemenata modificiranih eksperimentalnim biostaklima

[1] Health Center of Split-Dalmatia County, Vrgorac, Croatia
Dom zdravlja Splitsko-dalmatinske županije, Vrgorac, Hrvatska
[2] University of Zagreb School of Dental Medicine, Department of Endodontics and Restorative Dentistry, Gundulićeva 5, Zagreb, Croatia
Sveučilište u Zagrebu Stomatološki fakultet, Zavod za endodonciju i restaurativnu stomatologiju, Gundulićeva 5, Zagreb, Hrvatska
[3] Departamento de Odontología, Facultad de Ciencias de La Salud, Universidad CEU-Cardenal Herrera, Edificio Odontología, Avda del Pozo S/N, Alfara del Patriarca 46115, Valencia, Spain
Fakultet zdravstvenih znanosti, Odjel za stomatologiju, Sveučilište CEU-Cardenal Herrera, Edificio Odontología, Avda del Pozo S/N, Valencia, Španjolska
[4] Department of Therapeutic Dentistry, I.M. Sechenov First Moscow State Medical University, Moscow, Russia, 119146
Odjel za terapijsku stomatologiju, I.M. Sechenov First Moscow State Medical University, Moskva, Rusija
[5] University of Zagreb Faculty of Science, Department of Chemistry, Horvatovac 102a, 10000 Zagreb, Croatia
Sveučilište u Zagrebu, Prirodoslovno-matematički fakultet, Kemijski odsjek, Horvatovac 102 a, Zagreb, Hrvatska

Abstract

Objectives: The purpose of this *in vitro* study was to evaluate the effect of bioactive glasses containing a small proportion of fluoride and zinc in lower (BAG1) and higher ratios (BAG2) on the Vickers microhardness (VHN), surface morphology and chemical composition of high-viscosity glass ionomer cement and glass hybrid cement. **Materials and Methods:** Fuji IX (Fuji) and EQUIA Forte HT (Equia) were modified with 5 wt% BAG1 and BAG2. Six groups were prepared and stored in distilled water: Fuji, Fuji+ BAG1, Fuji+BAG2, Equia, Equia+ BAG1, and Equia+BAG2. BAG1 and BAG2 were characterized using FTIR. VHN was measured after 24 hours and 7 days. Representative samples from all groups were stored in phosphate buffered solution and analyzed using SEM-EDS. Data were analyzed using ANOVA and paired t-tests ($\alpha = 0.05$). **Results:** Fuji and Fuji+BAG1 showed the highest VHN at both time points, whereas BAG2 significantly reduced microhardness compared to original materials Fuji and Equia ($p<0.05$). All groups exhibited increased VHN over 7 days ($p<0.05$). FTIR confirmed the amorphous silicate and fluoride content. SEM-EDS confirmed the absence of crystalline precipitates on the material's surface when stored in phosphate containing solution. **Conclusions:** BAG1 preserved or slightly enhanced microhardness, while BAG2 significantly reduced it. There were no crystalline precipitates on original or on materials modified with 5 wt% bioactive glass. Optimizing BAG composition is essential to balance mechanical stability and bioactivity of glass ionomers.

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Address for correspondence
Ivan Šalinović
University of Zagreb, School of Dental Medicine
Department of Endodontics and Restorative Dentistry,
Gundulićeva 5, 10000 Zagreb, Croatia
Phone: +38514802126
isalinovic@sfzg.unizg.hr

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Antonela Šošić 0000-0001-9361-798X
Ivan Šalinović 0000-0002-5904-1427
Ivana Miletić 0000-0002-2864-150X
Ana Ivanišević 0000-0002-1380-0029
Ivana Kekez 0000-0001-8690-5465
Salvatore Sauro 0000-0002-2527-8776

Introduction

Glass ionomer cement (GIC) is a self-adhesive restorative material which was first described by Wilson and Kent in 1972 (1). Its two components include fluoroaluminosilicate glass powder and polyacrylic acid liquid, which may be copolymerized with carboxylic, maleic, tartaric, and itaconic acid to regulate the viscosity and stabilize the liquid (2). GIC bonds to the tooth structure via ionic interaction be-

Uvod

Staklenoionomerni cement (engl. *glass ionomer cement* – GIC) samoadhezivni je restaurativni materijal koji su prvi opisali Wilson i Kent 1972. godine (1). Njegove dvije komponente uključuju prašak fluoroaluminosilikatnoga stakla i tekućinu poliakrilne kiseline koja može biti kopolimerizirana s karboksilnom, maleinskom, vinskom i itakonskom kiselinom radi regulacije viskoznosti i stabilizacije tekućine (2).

tween the carboxyl groups of the polyacrylic acid and calcium in the hydroxyapatite crystals (3). These materials can also release other ions in the ionic exchange layer, e.g. fluorides, phosphates, silicates, aluminum, sodium, calcium and strontium (4,5). The ions released from GIC materials may interact and become incorporated into partially demineralized dental tissues (4,5). GICs exhibit cariostatic and caries-protective effects through the release of fluoride ions, making them the restorative material of choice for patients at high caries risk (5,6). Despite the advantages, the main drawback of GI materials is their inferior mechanical performance compared to composites (7). This was particularly true for early generations of GICs with high initial solubility when exposed to excess water, pronounced initial sensitivity to water loss when exposed to ambient air, poor mechanical properties, and low wear resistance, even after the material had matured (8,9).

The composition and properties of GIC have been substantially improved over the past few decades. An increased powder-to-liquid ratio and reduced particle size led to the development of high-viscosity glass ionomer cements (HVGIC) with improved mechanical properties compared with traditional glass ionomer cements (10). Although some HVGIC formulations demonstrate higher fluoride release, this effect is material-dependent and cannot be considered a universal characteristic of all HVGICs (11,12). Further mechanical improvements in glass hybrid material Equia Forte were achieved by modifying standard glass powder with ultrafine, highly reactive particles and high molecular weight polyacrylic acid, contributing to the strength of the material (13,14). Protection against early water contamination and further enhancement of mechanical properties, translucency, and marginal seal of the glass hybrid material were achieved by applying a nano-filled resin coating, Equia Forte coat (15–17). For Class I and smaller Class II posterior cavities, coated HVGIC and glass hybrid materials generally show similar clinical survival and retention to composite resins, though with inferior aesthetics and wear (15,18). These materials are a preferable choice for smaller long-term fillings when the cariostatic and remineralization effect is crucial, such as in high caries risk patients (19). However, the mechanical properties GICs are still inferior to the mechanical properties of composite resins (20). The resistance of dental restorative materials to deformation under functional forces is essential for a long-term clinical success. Evaluating mechanical properties such as Vickers microhardness (VHN) provides a practical and reliable approach for assessing the mechanical behavior of restorative materials and estimating their performance under functional loading conditions. (21).

The addition of bioactive glass (BAG) to GICs may affect the mechanical properties and the release of ions, which promote remineralization. It was shown that the addition of 5 wt% of BAG with 74% crystallinity improved the mechanical properties of GIs (22). Moreover, the bioactive and antimicrobial properties of BAG depend on its composition, structure, and ion-release kinetics, which is why BAG is increasingly used in dentistry (23). Zinc has been proven to exert antibacterial effect in ion-releasing materials, and the ad-

GIC se veže uz zubno tkivo na temelju ionske interakcije između karboksilnih skupina poliakrilne kiseline i kalcija u kristalima hidroksiapatita (3). Ti materijali također mogu otpuštati druge ione u sloju izmjene iona, primjerice, fluoride, fosfate, silikate, aluminij, natrij, kalcij i stroncij (4, 5). Ioni otpušteni iz GIC-a mogu uzajamno djelovati i biti ugrađeni u djelomično demineralizirana zubna tkiva (4, 5). GIC pokazuje kariostatski i karioprotektivni učinak otpuštanjem fluoridnih iona zbog čega je restaurativni materijal izbora za pacijente s visokim rizikom od karijesa (5, 6). Unatoč prednostima, glavni nedostatak staklenoionomernih materijala jest njihovo slabije mehaničko svojstvo u usporedbi s kompozitima (7). To je osobito bilo izraženo kod ranijih generacija GIC-a s visokom početnom topljivošću pri izlaganju višku vode, izraženom početnom osjetljivošću na gubitak vode pri izlaganju zraku, lošim mehaničkim svojstvima i niskom otpornošću na trošenje, čak i nakon sazrijevanja materijala (8, 9).

Sastav i svojstva GIC-a znatno su poboljšani tijekom posljednjih nekoliko desetljeća. Povećan omjer praška i tekućine, te smanjena veličina čestica rezultirali su razvojem staklenoionomernih cementa visoke viskoznosti (HVGIC) s boljim mehaničkim svojstvima u usporedbi s tradicionalnim staklenoionomernim cementima (10). Iako neke formulacije HVGIC-a pokazuju veće otpuštanje fluorida, taj je učinak ovisan o materijalu i ne može se smatrati univerzalnom značajkom svih HVGIC-a (11, 12). Daljnja mehanička poboljšanja staklohibridnoga materijala EQUIA Forte postignuta su modificiranjem standardnoga staklenoga praha ultrafininim, visoko reaktivnim česticama i poliakrilnom kiselinom velike molekulske mase, što pridonosi čvrstoći materijala (13, 14). Zaštita od rane kontaminacije vodom te dodatno poboljšanje mehaničkih svojstava, translucencije i rubnog brtvljenja staklohibridnoga materijala postignuti su primjenom nanopunjenoga smolastoga premaza EQUIA Forte Coat (15 – 17). Za kavitete klase I i manje kavitete klase II na stražnjim zubima, premazani HVGIC i staklohibridni materijali općenito pokazuju sličan klinički uspjeh i retenciju kao kompozitne smole, uz slabiju estetiku i otpornost na trošenje (15, 18). Ti su materijali poželjan izbor za manje dugotrajne ispune kada su kariostatski i remineralizacijski učinak ključni, primjerice kada je riječ o pacijentima s visokim rizikom od karijesa (19). Međutim, mehanička svojstva GIC-a i dalje su slabija od mehaničkih svojstava kompozitnih smola (20). Otpornost dentalnih restaurativnih materijala na deformaciju pod funkcionalnim silama ključna je za dugoročni klinički uspjeh. Procjena mehaničkih svojstava, poput Vickersove mikrotvrdoće (VHN), pruža praktičan i pouzdan pristup za procjenu mehaničkog ponašanja restaurativnih materijala i njihove izvedbe pod funkcionalnim opterećenjem (21).

Dodatak bioaktivnoga stakla (engl. *bioactive glass* – BAG) u GIC može utjecati na mehanička svojstva i otpuštanje iona koji potiču remineralizaciju. Dokazano je da dodatak 5 posto masenih postotaka (5 wt%) BAG-a sa 74 % kristaliničnosti poboljšava mehanička svojstva GIC-a (22). Nadalje, bioaktivna i antimikrobna svojstva BAG-a ovise o njegovu sastavu, strukturi i kinetici otpuštanja iona, zbog čega se BAG sve češće primjenjuje u stomatologiji (23). Pokazano je

dition of ZnO increased the mechanical properties of GICs (24). Even though the effect of the modification of GICs containing strontium, such as Fuji IX (GC, Tokyo, Japan) and Equia Forte HT Fil (GC, Tokyo, Japan), with experimental BAG containing zinc and fluoride improved ion release in neutral and acidic conditions (11), their effect on the microhardness and bioactivity has not been studied, according to the available literature.

Therefore, the aim of this study was to evaluate and compare the VHN, surface morphology, and chemical composition of high-viscosity glass ionomer Fuji IX GP® and glass hybrid cement EQUIA Forte HT Fil® modified with two types of bioactive glasses containing a small proportion of zinc and fluoride.

The null hypotheses of this study were that: (I) the modification of Fuji and Equia with experimental BAGs would not affect the microhardness; (II) VHN values at different time points would not differ significantly; (III) the modification of Fuji and Equia with BAG would not result in surface precipitates of calcium phosphates.

Materials and Methods

The research was approved by the Ethics Committee of the School of Dental Medicine, University of Zagreb, on March 12th in 2025 (Class: 003-01/25-05/03, Number: 251-60-4/51-5).

Commercially available encapsulated materials used in the study were: Fuji IX GP® (Fuji) (GC Corporation, Tokyo, Japan) and Equia forte HT Fil® (Equia) (GC Corporation, Tokyo, Japan) listed in Table 1.

Experimental powders of bioactive glass enriched with zinc containing fluoride were produced by melt-quenching

da cink djeluje antibakterijski u materijalima koji otpuštaju ione, a dodatak cinkova oksida (ZnO) povećava mehanička svojstva GIC-a (24). Iako je pokazano da modifikacija GIC-a koji sadržavaju stroncij, poput Fuji IX (GC, Tokio, Japan) i EQUIA-e Forte HT Fil (GC, Tokio, Japan), eksperimentalnim BAG-om koji sadrži cink i fluorid poboljšava otpuštanje iona u neutralnim i kiselim uvjetima (11), njihov učinak na mikrotvrdoću i bioaktivnost, prema dostupnoj literaturi, još nije istražen.

Stoga je cilj ove studije bio procijeniti i usporediti VHN, površinsku morfologiju i kemijski sastav visokoviskoznoga staklenoionomernog cementa Fuji IX GP® i staklohibridnoga cementa EQUIA Forte HT Fil® modificiranih dvjema vrstama bioaktivnih stakala koja sadržavaju mali udio cinka i fluorida.

Nulte hipoteze ove studije bile su sljedeće: (I) modifikacija Fujija i Equiaje eksperimentalnim BAG-ovima neće utjecati na mikrotvrdoću; (II) vrijednosti VHN-a u različitim vremenskim točkama neće se značajno razlikovati; (III) modifikacija Fujija i Equiaje BAG-om neće rezultirati površinskim precipitatima kalcijevih fosfata.

Materijali i metode

Istraživanje je odobrilo Etičko povjerenstvo Stomatološkog fakulteta Sveučilišta u Zagrebu, 12. ožujka 2025. (KLASA: 003-01/25-05/03, URBROJ: 251-60-4/51-5). Komercijalno dostupni kapsulirani materijali korišteni u studiji bili su: Fuji IX GP® (Fuji) (GC Corporation, Tokio, Japan) i EQUIA Forte HT Fil® (Equia) (GC Corporation, Tokio, Japan) i navedeni u su tablici 1. Eksperimentalni prašci bioaktivnoga stakla obogaćenoga cinkom i fluoridom proizvedeni su taljenjem i gašenjem oksidnih smjesa, nakon čega su slijedili brzo hlađenje, mljevenje i prosijavanje na < 30 μm, ka-

Table 1 Composition of commercial materials used in the study.
Tablica 1. Sastav komercijalnih materijala korištenih u studiji

Material and LOT number • Materijal i LOT broj	Manufacturer • Proizvođač	Powder composition • Sastav praha	Liquid composition • Sastav tekućine
Fuji IX® 250107A	GC, Tokyo, Japan	fluoroaluminosilicate glass, polyacrylic acid powder • Fluoroaluminosilikatno staklo, Prah poliakrilne kiseline	polyacrylic acid, polybasic carboxylic acid • Poliakrilna kiselina Polibazne karboksilne kiseline
Equia Forte HT Fil® 241212A	GC, Tokyo Japan	fluoroalumino silicate glass (92–97%), polyacrylic acid powder (3–8%), pigments (trace) • Fluoroaluminosilikatno staklo (92 –97 %), prah poliakrilne kiseline (3 –8 %), pigmenti (u tragovima)	polyacrylic acid (35–45%), polybasic carboxylic acid (5–10%), distilled water (45–55%) • Poliakrilna kiselina (35 –45 %), polibazne karboksilne kiseline (5 –10 %), destilirana voda (45 – 55 %)

Table 2 Composition of experimental BAG and BAG-F and powder components of Fuji IX and Equia Forte HT obtained by ICP MS analysis.
Tablica 2. Sastav eksperimentalnih materijala BAG i BAG-F te praškastih komponenti Fuji IX i Equia dobiven ICP-MS analizom

Material • Materijal	BAG1	BAG2	Fuji IX	Equia Forte
Component • Sastav	*w* / %	*w* / %	*w* / %	*w* / %
SiO_2	44.30	44.79	44.66	44.72
CaO	26.40	23.46	0.39	0.71
Na_2O	24.00	24.20	3.31	4.50
P_2O_5	3.90	2.50	2.11	2.10
SrO	0.40	1.01	35.99	31.26
Al_2O_3	-	0.79	10.27	13.51
ZnO	0.24	1.32	0.003	-
Total • Ukupno	99.24	98.07	96.73	96.80

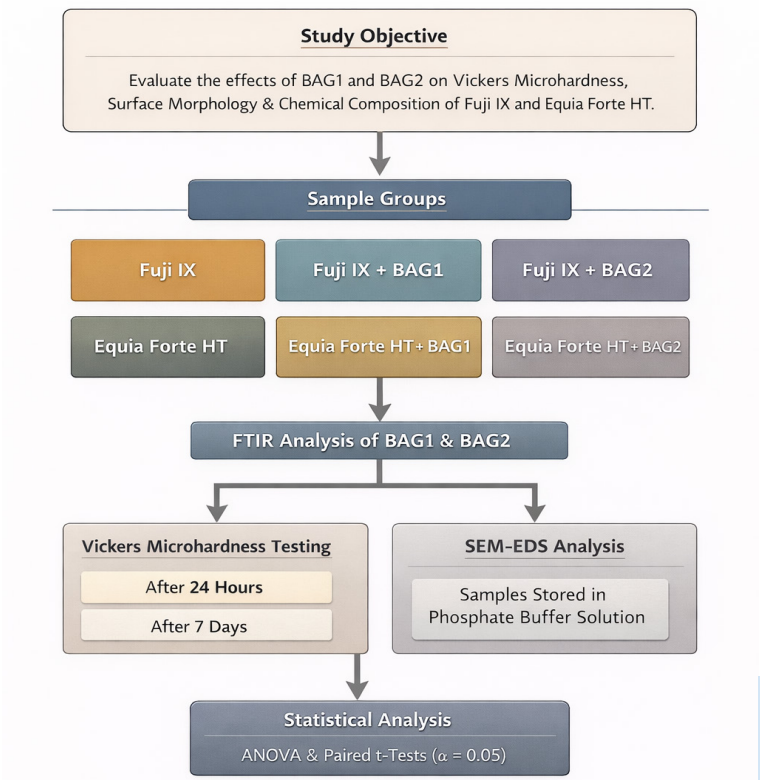


Figure 1 Flow chart illustrating experimental procedure taken in this study.
Slika 1. Dijagram tijeka koji prikazuje eksperimentalni postupak proveden u ovoj studiji

of oxide mixtures, followed by rapid cooling, grinding, and sieving < 30 μm as previously described (25–27).

The composition of the experimental glasses was confirmed using ICP MS as described in a previous research (11), and is presented in Table 2. The low percentage of compounds unidentified by ICP-MS is attributed to organic impurities and fluoride salts. In order to confirm that, in this experiment, FTIR spectra of BAG1 and BAG2 were recorded.

Experimental procedure is shown on a flow chart in *Figure 1 Flow chart illustrating experimental procedure taken in this study.*

Recording FTIR spectra

Infrared (IR) spectra of the solid samples 1 (BAG2) and 2 (BAG1) were recorded using a Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with an attenuated total reflectance (ATR) accessory. Spectra were collected in the 4000–200 cm^{-1} range at room temperature, with a spectral resolution of 4 cm^{-1}, averaging 32 scans per sample to improve the signal-to-noise ratio. The powdered sample 1 was analyzed directly in the solid state without additional preparation. In contrast, sample 2 contained larger particles and was therefore ground prior to measurement to ensure uniform contact with the ATR crystal.

Preparation of Samples

To prepare glass ionomer samples modified with BAGs, capsules of commercial materials were carefully opened using lower-molar extraction forceps to avoid damaging the membrane enclosing the fluid. Each capsule contained 0.4 g of powder. 5 wt% of glass powder was replaced with the same amount of experimental BAG powder.

ko je prethodno opisano (25 – 27). Sastav eksperimentalnih stakala potvrđen je ICP-MS analizom, kao što je opisano u prethodnom istraživanju (11) te je prikazan u tablici 2. Nizak udio spojeva koji nisu identificirani ICP-MS-om pripisuje se organskim nečistoćama i fluoridnim solima. Kako bi se to potvrdilo, u ovom su eksperimentu snimljeni FTIR spektri BAG1 i BAG2.

Eksperimentalni postupak prikazan je u dijagramu tijeka na slici 1.

Snimanje FTIR spektra

Infracrveni (IR) spektri čvrstih uzoraka 1 (BAG2) i 2 (BAG1) snimljeni su FTIR spektrometrom Thermo Scientific Nicolet iS50 opremljenim ATR dodatkom. Spektri su prikupljani u području od 4000 do 200 cm^{-1} pri sobnoj temperaturi, sa spektralnom rezolucijom od 4 cm^{-1}, uz prosjek od 32 skena po uzorku radi poboljšanja omjera signal/šum. Praškasti uzorak 1 analiziran je izravno u čvrstom stanju, bez dodatne pripreme. Nasuprot tomu, uzorak 2 sadržavao je veće čestice te je prije mjerenja samljeven kako bi se osigurao ujednačeni kontakt s ATR kristalom.

Priprema uzoraka

Za pripremu uzoraka staklenoionomernih cementa modificiranih BAG-om, kapsule komercijalnih materijala pažljivo su otvorene s pomoću ekstrakcijskih kliješta za donje kutnjake da bi se izbjeglo oštećenje membrane koja obavija tekućinu. Svaka kapsula sadržavala je 0,4 g praha. Pet posto

The capsules of commercial and experimental materials modified with 5 wt% BAG were activated and mixed in 3M™ ESPE™ CapMixTM (3M ESPE, Seefeld, Germany) for 10 s, according to the manufacturer's instructions, and the samples were prepared using cylindrical Teflon molds 8 mm width x 2 mm height (*17*). To avoid air trapping, polyester strips were placed under the mold on a glass tile, and the material was gently compressed on both sides of the mold by glass. The samples were left to set for one hour. Subsequently, they were gently removed from the molds. Surfaces of the samples were wet polished and leveled for 20s with silicone carbide discs numbered 320, 800 and 1200, respectively (Metkon Gripo 2V Grinder/Polisher, Metkon Instruments Inc., Bursa, Turkey). Each material sample was transferred to a vial containing 5ml of distilled water.

There were six groups of materials: 1. Fuji, F; 2 Equia, E; 3 Fuji+BAG1, FB1; 4 Fuji IX+BAG2, FB2; 5 Equia+BAG1, EB1; 6. Equia+BAG2, EB2

Microhardness Testing

The Vickers hardness measurements were performed in triplicate, 24 hours and 7 days after mixing, on the marked surface.

The Vickers microhardness (VHN) was determined using a microhardness tester (CSV-10; ESI Prüftechnik GmbH, Wendlingen, Germany) with a load of 50 g and a dwell time of 10 s. A diamond indenter of defined geometry - a square-based pyramid with a 136° angle between opposite faces - was applied to the material surface, and the dimensions of the resulting indentation were measured to calculate the VHN. Before the measurements, samples were left to dry on a paper tissue for a minimum of 60 minutes. Between measurements, samples were stored in distilled water.

SEM-EDS evaluation

For each experimental group, one sample was stored in PBS (phosphate-buffered saline) for 45 days, vacuum-dried for 10 days, and subjected to SEM-EDS analysis. Surface imaging was performed using a JSM-7000F microscope (JEOL Ltd., Tokyo, Japan) operated at 5 kV, with a 10 mm working distance and magnifications of 500×, 1000×, and 5000×. Elemental data were obtained using an Inca 350 EDS system (Oxford Instruments, High Wycombe, UK). Samples were brushed gently to remove loose particles and then air-dried before analysis. This preparation more clearly revealed the surface topography and enabled the EDS system to identify the present elements with greater confidence.

Statistical Analysis of Microhardness Data

The statistical analysis was conducted using SPSS version 21 (IBM SPSS Statis Armonk, NY, USA). A priori power analysis for an ANOVA with fixed effects was performed using G*Power software (version 3.1.9.6). The effect size was estimated from the pilot study data, i.e., the group mean and the pooled standard deviation. For an effect size of 0.8, a significance level of 0.05, 6 groups, and a desired power of 0.85,

masenih postotaka (5wt %) staklenoga praha zamijenjeno je jednakom masom eksperimentalnog BAG praha.

Kapsule komercijalnih i eksperimentalnih materijala modificiranih s 5 masenih postotaka (5 wt %) BAG-a aktivirane su i miješane u uređaju 3M™ ESPE™ CapMixTM (3M ESPE, Seefeld, Njemačka) tijekom 10 sekundi prema uputama proizvođača, a uzorci su izrađeni s pomoću cilindričnih teflonskih kalupa dimenzija 8 mm širine i 2 mm visine (17). Da bi se izbjeglo zadržavanje zraka, poliesterske trakice postavljene su ispod kalupa na staklenu ploču, a materijal je nježno pritisnut staklom s obje strane kalupa. Uzorci su ostavljeni da se stvrdnjavaju jedan sat i zatim su pažljivo izvađeni iz kalupa. Površine uzoraka mokro su polirane i izravnane tijekom 20 sekundi s pomoću silicij-karbidnih diskova granulacije 320, 800 i 1200 (Metkon Gripo 2V Grinder/Polisher, Metkon Instruments Inc., Bursa, Turska). Svaki uzorak materijala prenesen je u posudicu koja je sadržavala 5 mL destilirane vode.

Pripremljeno je šest skupina materijala: Fuji, F; Equia, E; Fuji + BAG1, FB1; Fuji IX + BAG2, FB2; Equia + BAG1, EB1; Equia + BAG2, EB2

Ispitivanje mikrotvrdoće

Mjerenja Vickersove tvrdoće provedena su u trostrukom ponavljanju poslije 24 sata i poslije 7 dana nakon miješanja, na označenoj površini.

Vickersova mikrotvrdoća (VHN) određena je pomoću uređaja za mikrotvrdoću (CSV-10; ESI Prüftechnik GmbH, Wendlingen, Njemačka) s opterećenjem od 50 g i vremenom opterećenja od 10 sekundi. Na površinu materijala djelovao je dijamantni penetrator definirane geometrije – piramida s četvrtastom bazom i kutom od 136° između suprotnih ploha – a dimenzije nastaloga otiska izmjerene su radi izračuna VHN-a. Prije mjerenja uzorci su ostavljeni da se suše na papirnatom ubrusu najmanje 60 minuta. Između mjerenja uzorci su bili pohranjeni u destiliranoj vodi.

SEM-EDS analiza

Za svaku eksperimentalnu skupinu jedan je uzorak pohranjen u PBS-u tijekom 45 dana, zatim vakuumski sušen 10 dana i podvrgnut SEM-EDS analizi. Površinsko snimanje provedeno je pomoću mikroskopa JSM-7000F (JEOL Ltd., Tokio, Japan) pri 5 kV, radnoj udaljenosti od 10 mm i povećanjima od 500, 1000 i 5000 puta. Elementarni podatci dobiveni su s pomoću EDS sustava Inca 350 (Oxford Instruments, High Wycombe, UK). Prije analize uzorci su nježno očišćeni četkicom radi uklanjanja labavih površinskih čestica, a zatim osušeni na zraku. Ta priprema jasnije je prikazala površinsku topografiju i omogućila sustavu EDS da s većom pouzdanošću identificira prisutne elemente.

Statistička analiza podataka o mikrotvrdoći

Statistička analiza obavljena je u programu SPSS verzija 21 (IBM SPSS Statistics, Armonk, NY, SAD). A priori analiza snage za analizu varijance s fiksnim učincima provedena je u programu G*Power (verzija 3.1.9.6). Veličina učinka procijenjena je iz podataka pilot-studije, odnosno iz srednje vrijednosti skupina i združenoga standardnog odstupanja. Za veličinu učinka 0,8, razinu značajnosti 0,05, 6 skupina i že-

the minimum required sample size is 5 per group, yielding an actual power of 0.871. The chosen sample size was in accordance with what has been reported in previous studies (28–30). The normality of distribution was tested using the Shapiro-Wilk test, and homogeneity of variance using Levene's test. The microhardness data at one time point were analyzed using analysis of variance (ANOVA) and post hoc Least Significant Difference (LSD) test with Bonferroni correction, the level of significance was set at $\alpha = 0.05$. A paired t-test was used to compare one group at different time points.

Results

FTIR spectra

The ATR-FTIR spectra of samples 1 (BAG2) and 2 (BAG1) (Figure 2) exhibit the characteristic vibrational features of amorphous silicate and fluorosilicate materials. Both spectra display a strong, broad absorption band centered around 1070–1080 cm^{-1}, attributed to the asymmetric stretching vibration of Si–O–Si linkages within the silicate network. The results are presented in Figure 1.

Compared with sample 1, sample 2 shows a slight shift of the main band toward lower wavenumbers and a reduction in its relative intensity, suggesting minor variations in network connectivity or in the local chemical environment of the silicate structure. The low-frequency region (below 800 cm^{-1}) also exhibits minor differences in band shape, including a broader feature between 700 and 750 cm^{-1}, which may reflect subtle structural or compositional effects.

Both spectra show a weak, broad absorption in the 2800–3000 cm^{-1} region, attributed to surface hydroxyl groups or trace amounts of adsorbed organic species, and a bending vibration near 460 cm^{-1}, corresponding to Si–O–Si deformation modes. The absence of sharp peaks across the entire spectral range indicates that both samples are amorphous glass powders.

Overall, the spectra of BAG1 and BAG2 are qualitatively similar, with only minor shifts and intensity differences, implying comparable silicate frameworks with slight variations in local bonding and network organization.

Microhardness analysis

ANOVA analysis showed statistically significant differences in microhardness values between experimental groups at a particular time point (24 hours and 7 days).

ljenu snagu od 0,85, minimalni potreban uzorak iznosio je 5 po skupini, uz stvarnu snagu od 0,871. Odabrana veličina uzorka bila je u skladu s do sada objavljenim studijama (28 – 30). Normalnost raspodjele testirana je Shapiro-Wilkovim testom, a homogenost varijanci Leveneovim testom. Podatci o mikrotvrdoći za jednu vremensku točku analizirani su analizom varijance (ANOVA) i post hoc LSD testom uz Bonferronijevu korekciju, pri čemu je razina značajnosti postavljena na $\alpha = 0,05$. Upareni t-test korišten je za usporedbu iste skupine u različitim vremenskim točkama.

Rezultati

FTIR spektar

ATR-FTIR spektri uzoraka 1 (BAG2) i 2 (BAG1) (slika 2.) pokazuju karakteristične vibracijske značajke amorfnih silikatnih i fluorosilikatnih materijala. Oba spektra prikazuju snažnu, široku apsorpcijsku vrpcu centriranu od 1070 do 1080 cm^{-1} koja se pripisuje asimetričnoj vibraciji istezanja Si – O – Si veza unutar silikatne mreže. Rezultati se nalaze na slici 1.

U usporedbi s uzorkom 1, uzorak 2 pokazuje blagi pomak glavne vrpce prema nižim valnim brojevima te smanjenje njezina relativnog intenziteta, što upućuje na manje varijacije u povezanosti mreže ili u lokalnom kemijskom okruženju silikatne strukture. Niskofrekventno područje (ispod 800 cm^{-1}) također pokazuje manje razlike u obliku vrpci, uključujući širu značajku između 700 i 750 cm^{-1}, što može odražavati suptilne strukturne ili sastavne učinke. Oba spektra pokazuju slabu, široku apsorpciju u području od 2800 do 3000 cm^{-1} koja se pripisuje površinskim hidroksilnim skupinama ili tragovima adsorbiranih organskih vrsta, te savojnu vibraciju oko 460 cm^{-1} koja odgovara deformacijskim modulima Si – O– Si veza. Odsutnost oštrih vrhova kroz cijelo spektralno područje upućuje na to da su oba uzorka amorfni stakleni prašci.

Općenito, spektri BAG1 i BAG2 kvalitativno su slični, uz samo manje pomake i razlike u intenzitetu, što upućuje na usporedive silikatne mreže s blagim razlikama u lokalnom vezanju i organizaciji strukture.

Ispitivanje mikrotvrdoće

ANOVA analiza pokazala je statistički značajne razlike u vrijednostima mikrotvrdoće između eksperimentalnih skupina u određenim vremenskim točkama (24 sata i 7 dana).

Table 3 Microhardness values and standard deviations for 6 experimental groups.
Tablica 3. Vrijednosti mikrotvrdoće i standardne devijacije za 6 eksperimentalnih skupina

Group • Skupina	Mean+standard deviation • Medijan +standardna devijacija (24h)	Mean+standard deviation • Medijan +standardna devijacija (7d)
Fuji IX	50.634^{ab}±5.671	64.48^{a}±6.793
Fuji IX +BAG1	53.163^{a}±5.422	63.443^{a}± 4.124
FujI IX +BAG2	38.433^{c}±7.559	49.133^{b}±5.873
Equia Forte	41.2^{bc}±6.850	46.833^{b}±5.595
Equia Forte +BAG1	40.547^{c}±6.774	45.896^{b}±7.189
Equia Forte +BAG2	23.72^{d}±10.030	30.205^{c}±6.022

*Different superscript letters indicate statistically significant differences among groups. There are no statistically significant differences between groups with the same letter. • Različiti eksponenti označavaju statistički značajne razlike između skupina. Ne postoje statistički značajne razlike između skupina s istim slovom.

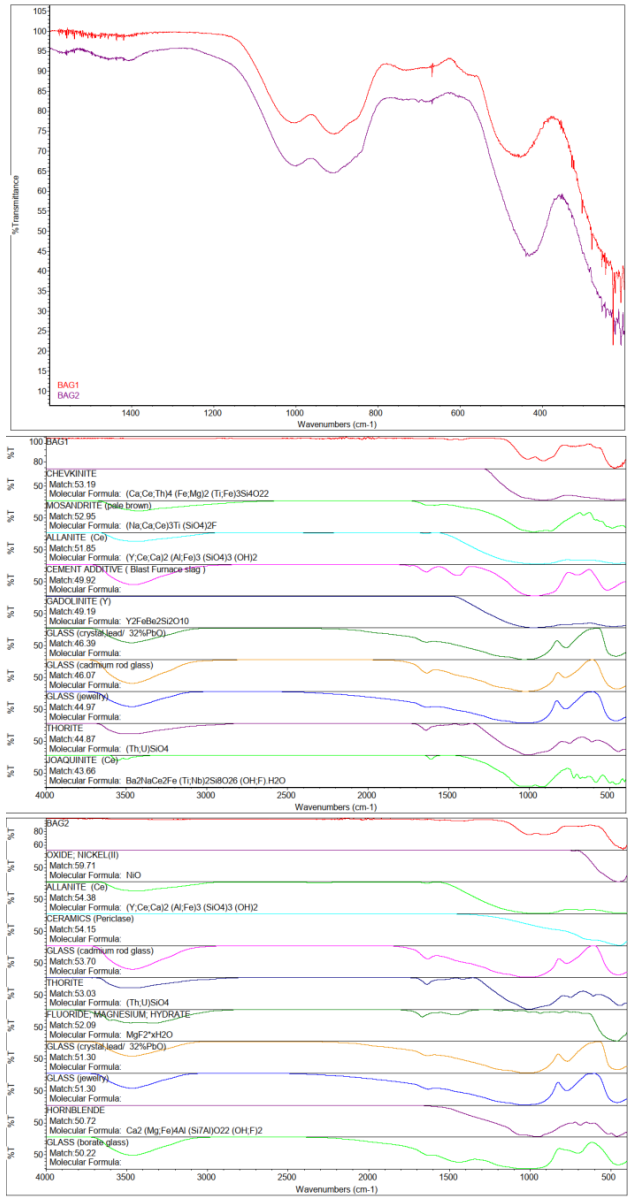


Figure 2 FTIR analysis of experimental bioactive glass; a) Overlap of BAG1 and BAG2 spectra, b) Composition of BAG1, c) Composition of BAG2.
Slika 2. FTIR analiza eksperimentalnog bioaktivnog stakla; a) preklapanje spektara BAG1 i BAG2, b) sastav BAG1, c) sastav BAG2

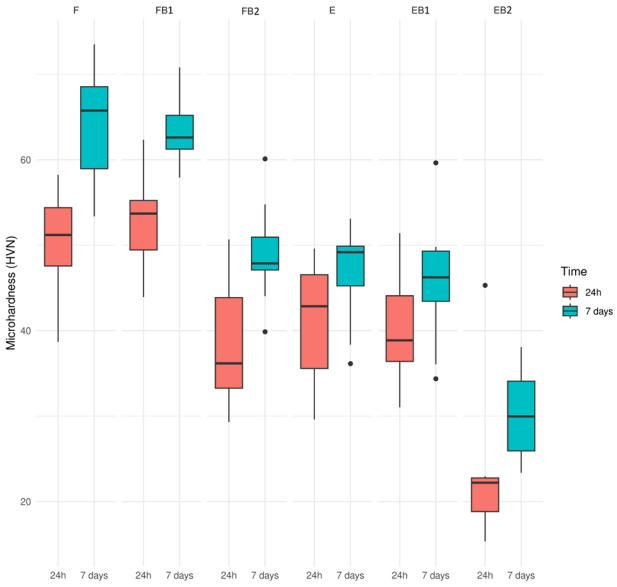
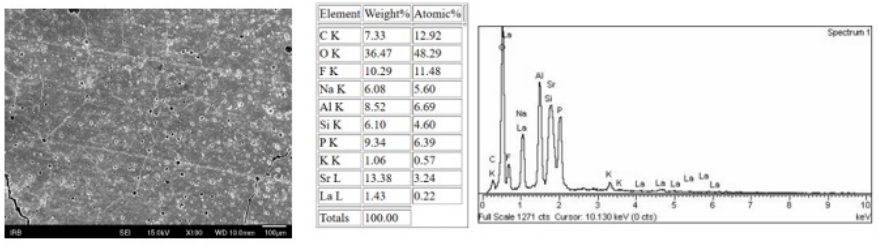
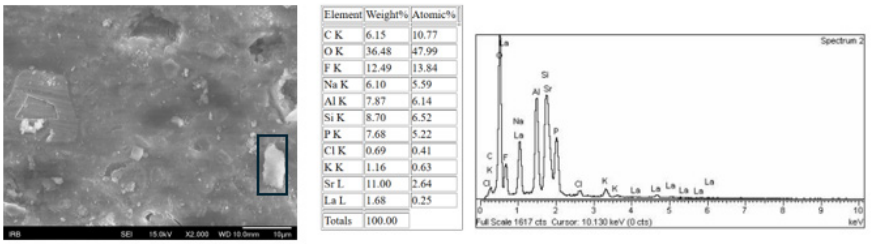


Figure 3 Comparative boxplot diagram of microhardness after 24h and 7 days.
Slika 3. Usporedni kutijasti dijagram (boxplot) mikrotvrdoće poslije 24 sata i poslije 7 dana



Element	Weight%	Atomic%
C K	7.33	12.92
O K	36.47	48.29
F K	10.29	11.48
Na K	6.08	5.60
Al K	8.52	6.69
Si K	6.10	4.60
P K	9.34	6.39
K K	1.06	0.57
Sr L	13.38	3.24
La L	1.43	0.22
Totals	100.00	

A)

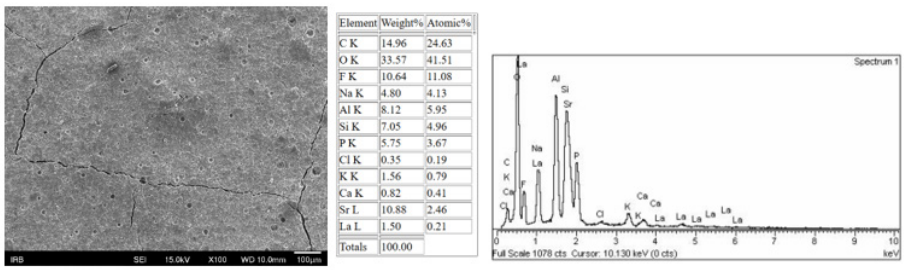


Element	Weight%	Atomic%
C K	6.15	10.77
O K	36.48	47.99
F K	12.49	13.84
Na K	6.10	5.59
Al K	7.87	6.14
Si K	8.70	6.52
P K	7.68	5.22
Cl K	0.69	0.41
K K	1.16	0.63
Sr L	11.00	2.64
La L	1.68	0.25
Totals	100.00	

B)

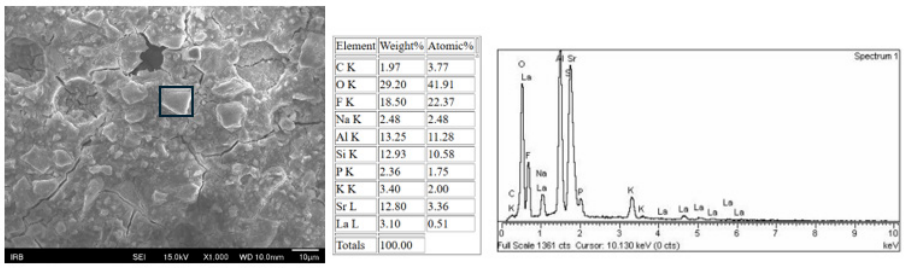
Figure 4 SEM EDS analysis of Equia sample at magnification of 100x shows strontium-aluminosilicate composition (A). SEM-EDS analysis of surface forms at 2000x magnification showed a composition identical to that of the whole sample (B).

Slika 4. SEM-EDS analiza uzorka Equia pri povećanju od 100 puta pokazuje stroncij-aluminosilikatni sastav (A); SEM-EDS analiza površinskih struktura pri povećanju od 200 puta pokazala je sastav identičan ukupnom uzorku (B)



Element	Weight%	Atomic%
C K	14.96	24.63
O K	33.57	41.51
F K	10.64	11.08
Na K	4.80	4.13
Al K	8.12	5.95
Si K	7.05	4.96
P K	5.75	3.67
Cl K	0.35	0.19
K K	1.56	0.79
Ca K	0.82	0.41
Sr L	10.88	2.46
La L	1.50	0.21
Totals	100.00	

(A)

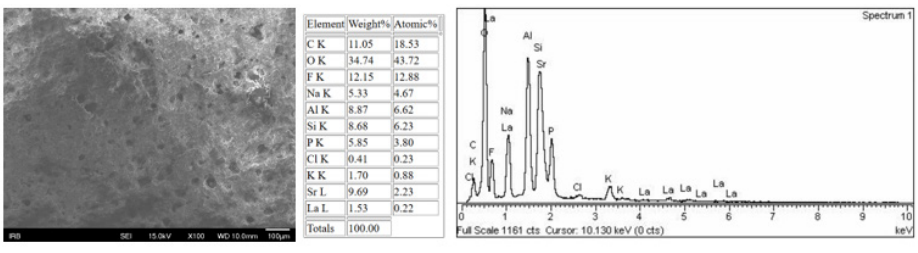


Element	Weight%	Atomic%
C K	1.97	3.77
O K	29.20	41.91
F K	18.50	22.37
Na K	2.48	2.48
Al K	13.25	11.28
Si K	12.93	10.58
P K	2.36	1.75
K K	3.40	2.00
Sr L	12.80	3.36
La L	3.10	0.51
Totals	100.00	

(B)

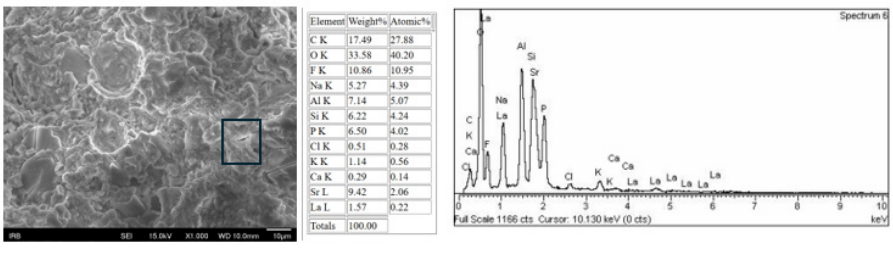
Figure 5 SEM EDS analysis of Equia+BAG1 sample showed visible cracks and surface defects because of the evaporation of inherent water. Ca was identified in Equia+BAG1 sample because of modification with BAG1 (A). At a magnification of 1000 times, strontium-fluoroaluminosilicate glass particles were identified near the surface (B).

Slika 5. SEM-EDS analiza uzorka Equia + BAG1 pokazala je vidljive pukotine i površinske defekte zbog isparavanja inherentne vode; Ca je identificiran u uzorku Equia + BAG1 zbog modifikacije s BAG1 (A); pri povećanju od 1000 puta uočene su čestice stroncij-fluoroaluminosilikatnoga stakla u blizini površine (B)



Element	Weight%	Atomic%
C K	11.05	18.53
O K	34.74	43.72
F K	12.15	12.88
Na K	5.33	4.67
Al K	8.87	6.62
Si K	8.68	6.23
P K	5.85	3.80
Cl K	0.41	0.23
K K	1.70	0.88
Sr L	9.69	2.23
La L	1.53	0.22
Totals	100.00	

(A)

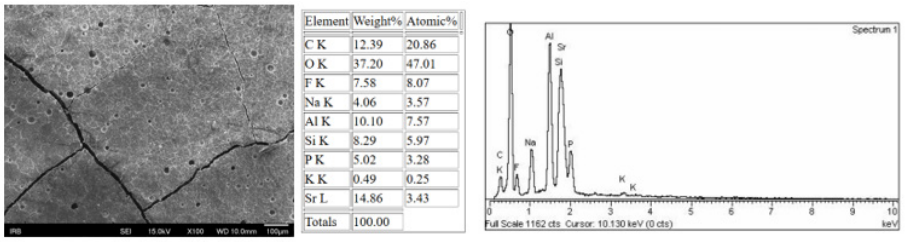


Element	Weight%	Atomic%
C K	17.49	27.88
O K	33.58	40.20
F K	10.86	10.95
Na K	5.27	4.39
Al K	7.14	5.07
Si K	6.22	4.24
P K	6.50	4.02
Cl K	0.51	0.28
K K	1.14	0.56
Ca K	0.29	0.14
Sr L	9.42	2.06
La L	1.57	0.22
Totals	100.00	

(B)

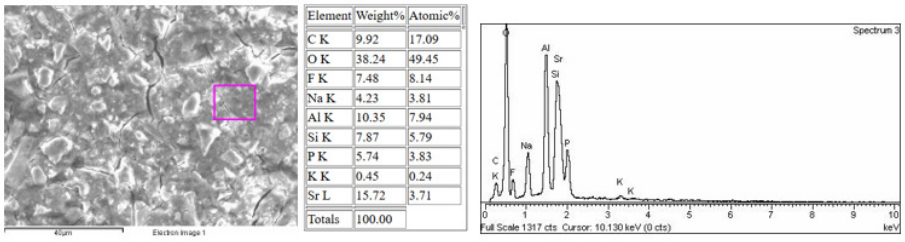
Figure 6 SEM EDS analysis of Equia+BAG2 samples at the magnification of 100 X showed a smooth surface and contents similar to the original Equia formulation with higher fluoride levels (A). At the magnification of 1000 X low levels of calcium originating form BAG2 were detected as an integral part of the cement sample (B).

Slika 6. SEM-EDS analiza uzoraka Equia + BAG2 pri povećanju od 100 puta pokazala je glatku površinu i sastav sličan izvornoj formulaciji Equiaje, uz više razine fluorida (A); pri povećanju od 1000 puta detektirane su niske razine kalcija podrijetlom iz BAG-a 2 kao dio cementnog uzorka (B)



Element	Weight%	Atomic%
C K	12.39	20.86
O K	37.20	47.01
F K	7.58	8.07
Na K	4.06	3.57
Al K	10.10	7.57
Si K	8.29	5.97
P K	5.02	3.28
K K	0.49	0.25
Sr L	14.86	3.43
Totals	100.00	

(A)

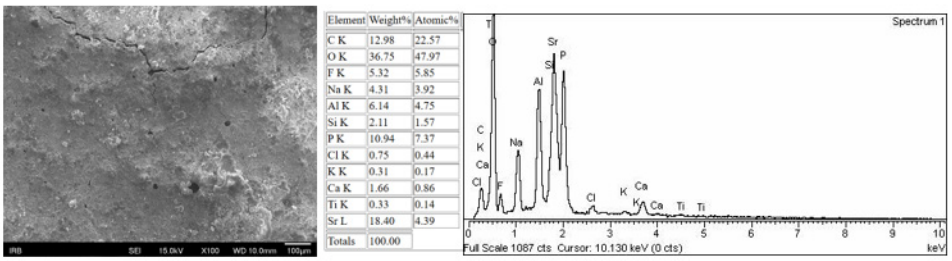


Element	Weight%	Atomic%
C K	9.92	17.09
O K	38.24	49.45
F K	7.48	8.14
Na K	4.23	3.81
Al K	10.35	7.94
Si K	7.87	5.79
P K	5.74	3.83
K K	0.45	0.24
Sr L	15.72	3.71
Totals	100.00	

(B)

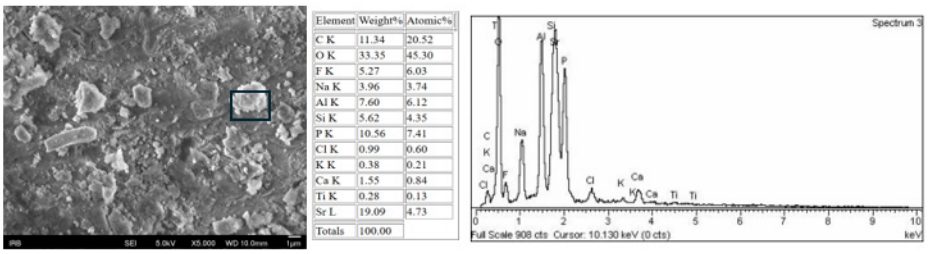
Figure 7 SEM EDS analysis of Fuji at 100 X magnification showed a smooth surface with cracks and surface defects due to the vacuum drying procedure. Fuji composition corresponded to strontium-fluoroaluminosilicate (A). Glass particles near the surface correspond to silicate particles form fluoroaluminosiliacte glass filler of the Fuji material (B).

Slika 7. SEM-EDS analiza uzorka Fuji pri povećanju od 100 puta pokazala je glatku površinu s pukotinama i površinskim defektima zbog vakuumskog sušenja; sastav materijala Fuji odgovara stroncij-fluoroaluminosilikatu (A); staklene čestice u blizini površine odgovaraju silikatnim česticama fluoroaluminosilikatnoga staklenog punila materijala Fuji (B)



Element	Weight%	Atomic%
C K	12.98	22.57
O K	36.75	47.97
F K	5.32	5.85
Na K	4.31	3.92
Al K	6.14	4.75
Si K	2.11	1.57
P K	10.94	7.37
Cl K	0.75	0.44
K K	0.31	0.17
Ca K	1.66	0.86
Ti K	0.33	0.14
Sr L	18.40	4.39
Totals	100.00	

A

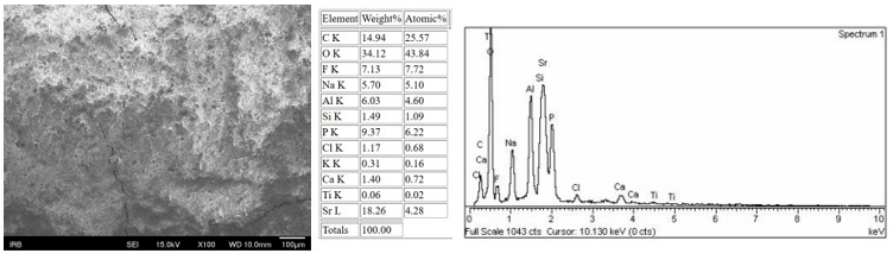


Element	Weight%	Atomic%
C K	11.34	20.52
O K	33.35	45.30
F K	5.27	6.03
Na K	3.96	3.74
Al K	7.60	6.12
Si K	5.62	4.35
P K	10.56	7.41
Cl K	0.99	0.60
K K	0.38	0.21
Ca K	1.55	0.84
Ti K	0.28	0.13
Sr L	19.09	4.73
Totals	100.00	

B

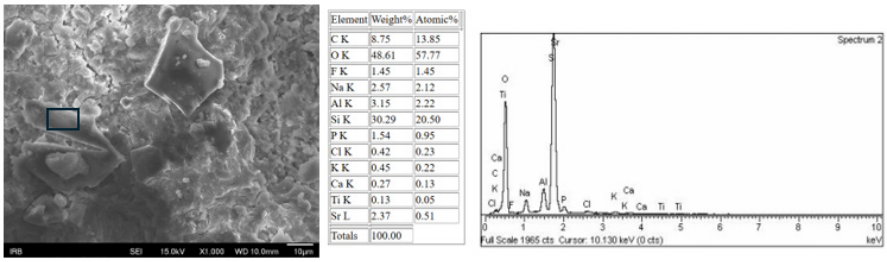
Figure 8 SEM EDS analysis of the Fuji+BAG1 sample at a magnification of 100 X showed more Ca content and less F and Al, when compared to the Fuji sample (Figure 5 A). Impurities on the surface at magnification 5000 X had a similar composition to the sample at a larger scale (B).

Slika 8. SEM-EDS analiza uzorka Fuji + BAG1 pri povećanju od 100 puta pokazala je veći sadržaj Ca te niži sadržaj F i Al u usporedbi s uzorkom Fuji (A); nečistoće na površini pri povećanju od 5000 puta imale su sličan sastav kao i uzorak na većoj ljestvici (B)



Element	Weight%	Atomic%
C K	14.94	25.57
O K	34.12	43.84
F K	7.13	7.72
Na K	5.70	5.10
Al K	6.03	4.60
Si K	1.49	1.09
P K	9.37	6.22
Cl K	1.17	0.68
K K	0.31	0.16
Ca K	1.40	0.72
Ti K	0.06	0.02
Sr L	18.26	4.28
Totals	100.00	

A



Element	Weight%	Atomic%
C K	8.75	13.85
O K	48.61	57.77
F K	1.45	1.45
Na K	2.57	2.12
Al K	3.15	2.22
Si K	30.29	20.50
P K	1.54	0.95
Cl K	0.42	0.23
K K	0.45	0.22
Ca K	0.27	0.13
Ti K	0.13	0.05
Sr L	2.37	0.51
Totals	100.00	

B

Figure 9 SEM EDS analysis of Fuji+BAG2 sample showed slightly higher fluoride content, and detectable calcium levels (A). Glass particles near the surface correspond to silicate particles form fluoroaluminosiliacte glass filler of the Fuji material (B).

Slika 9. SEM-EDS analiza uzorka Fuji + BAG2 pokazala je nešto viši sadržaj fluorida te detektabilne razine kalcija (A); staklene čestice u blizini površine odgovaraju silikatnim česticama fluoroaluminosilikatnoga staklenog punila materijala Fuji (B)

ANOVA analysis showed high statistically significant differences between groups at both time points: $p < 0.00001$ at both 24 hours and 7 days after mixing. The results of the LSD test indicated a clear ranking of microhardness between the groups.

Mean microhardness values and standard deviations for 6 experimental groups after 24 hours and after seven days are presented in Table 3. After 24 hours, Fuji+BAG1 samples showed the highest microhardness (53.16) followed by Fuji (50.63). Equia+BAG2 group had the lowest values (23.72). After 7 days, microhardness increased significantly in almost all groups, with the highest values recorded in groups Fuji (64.48) and Fuji+BAG1 (63.44), whereas the Equia+BAG2 group remained the weakest (30.20).

Within the same group, microhardness values at different time points were compared; differences were statistically significant for groups Fuji, Fuji+BAG1, Fuji+BAG2, and Equia (p-values 0.0001871, 0.0005441, 0.0006575, 0.004463, respectively), and microhardness was higher at the second time point. For groups Equia+BAG2 and Equia+BAG1, microhardness did not significantly change over time (p-values of 0.2746 and 0.08398, respectively) (Figure 3).

SEM-EDS

SEM EDS analysis of Equia sample at lower magnification corresponded to the declared Equia composition of fluoroaluminosilicate glass where calcium was replaced by strontium (Figure 4A). Surface defects are observed. An analysis at higher magnification showed that amorphous structures at the surface correspond to the sample composition (Figure 4B).

The SEM EDS analysis of Equia+BAG1 sample showed visible cracks and surface defects, but Ca was also noticed in the composition (Figure 5A). In 1000x magnification strontium-fluoroaluminosilicate glass particles are observed near the sample's surface (Figure 5B).

Equia+BAG2 samples showed a smooth surface and contents similar to the original formulation, but with slightly higher fluoride levels (Figure 6A). Low levels of calcium were also detected as an integral part of the cement sample (Figure 6B).

SEM-EDS analysis of Fuji revealed a smooth surface with cracks and surface defects. Fuji composition was similar to Equia original formulation (Figure 7A, B).

Fuji+BAG1 sample exhibited more Ca content, and less F and Al than Fuji, surface irregularities are observed (Figure 8A). The composition of the impurities on the surface corresponds to the sample's overall composition (Figure 8B).

The analysis showed slightly higher fluoride content and detectable calcium levels in Fuji+BAG2 sample (Figure 9A). Glass particles near the surface corresponded to silicate particles form fluoroaluminosiliacte glass filler of the Fuji material (Figure 9B).

Discussion

The results of the present study showed that the modification of high viscosity GIC and glass hybrid material with bioactive glass containing a lower percentage of ZnO and flu-

ANOVA analiza pokazala je statistički značajne razlike između skupina u obje vremenske točke: $p < 0,00001$ poslije 24 sata i poslije 7 dana od miješanja. Rezultati LSD testa upućivali su na jasan poredak mikrotvrdoće između skupina.

Srednje vrijednosti mikrotvrdoće i standardne devijacije za šest eksperimentalnih skupina poslije 24 sata i poslije sedam dana prikazane su u tablici 3. Poslije 24 sata uzorci Fuji + BAG1 pokazali su najveću mikrotvrdoću (53, 16), a slijedila ih je skupina Fuji (50, 63). Skupina Equia + BAG2 imala je najniže vrijednosti (23, 72). Poslije 7 dana mikrotvrdoća se značajno povećala u gotovo svim skupinama, pri čemu su najviše vrijednosti zabilježene u skupinama Fuji (64, 48) i Fuji + BAG1 (63, 44), a skupina Equia + BAG2 i dalje je imala najniže vrijednosti (30, 20).

Unutar iste skupine uspoređene su vrijednosti mikrotvrdoće u različitim vremenskim točkama te su razlike bile statistički značajne za skupine Fuji, Fuji + BAG1, Fuji + BAG2 i Equia (p-vrijednosti 0,0001871; 0,0005441; 0,0006575; 0,004463), pri čemu je mikrotvrdoća bila viša u drugoj vremenskoj točki. Za skupine Equia + BAG2 i Equia + BAG1 nije uočen statistički značajan porast mikrotvrdoće tijekom vremena (p-vrijednosti 0,2746 i 0,08398) (slika 3.).

SEM-EDS

SEM-EDS analiza uzorka Equia pri manjem povećanju odgovara deklariranom sastavu toga materijala, odnosno fluoroaluminosilikatnom staklu u kojemu je kalcij zamijenjen stroncijem (slika 4. A). Na površini su uočeni defekti. Analiza pri većem povećanju pokazuje da amorfne strukture na površini odgovaraju sastavu uzorka (slika 4. B).

SEM-EDS analiza uzorka Equia + BAG1 pokazala je vidljive pukotine i površinske defekte, pri čemu je u sastavu također detektiran kalcij (slika 5. A). Pri povećanju od 1000 puta uočene su čestice stroncij-fluoroaluminosilikatnoga stakla u blizini površine uzorka (slika 5. B).

Uzorci Equia + BAG2 pokazali su glatku površinu i sastav sličan izvornoj formulaciji, ali uz nešto višu razinu fluorida (slika 6. A). Također su uočene niske razine kalcija kao dio cementnog uzorka (slika 6. B).

SEM-EDS analiza uzorka Fuji otkrila je glatku površinu s pukotinama i površinskim defektima. Sastav materijala Fuji bio je sličan izvornoj formulaciji Equiaje (slika 7. A i B).

Uzorak Fuji + BAG1 pokazao je veći sadržaj kalcija te niži sadržaj željeza i aluminija u usporedbi s Fujijem, uz prisutne površinske nepravilnosti (slika 8. A). Sastav nečistoća na površini odgovara ukupnom sastavu uzorka (slika 8. B).

Analiza uzorka Fuji + BAG2 pokazala je nešto viši sadržaj fluorida i detektabilne razine kalcija (slika 9. A). Staklene čestice u blizini površine odgovaraju silikatnim česticama fluoroaluminosilikatnoga staklenoga punila materijala Fuji (slika 9. B).

Rasprava

Rezultati ove studije pokazali su da modifikacija visoko viskoznoga GIC-a i stakleno-hibridnoga materijala bioaktivnim staklom koje sadrži niži postotak cinkova oksida i fluo-

orides (BAG1) did not significantly affect microhardness after 24 h and 7 days. On the contrary, the modification with bioactive glass containing more fluorides (BAG2) significantly reduced microhardness in both materials. Considering microhardness over time, the increase was observed in all groups, and it was significant in commercial and experimental formulations. Thus, the null hypotheses were rejected.

Although several studies have compared the microhardness of GIC based materials (31–33), limited research has investigated changes in surface microhardness of these materials when modified with bioactive glass (34). The effects of the BAG1 and BAG2 modifications on GIC microhardness can be explained by differences in Fuji IX and Equia compositions and by the influence of bioactive glass on the setting process. Namely, the setting mechanism of GIC includes hydration of powder particles and cross-linking of carboxyl groups of polyalkenoic acid with released ions (Sr^{2+} and Al^{3+}), after which silica-gel is formed. Slow-moving Al^{3+} ions enter the aqueous medium and cross-link polyacrylic acid chains, displacing Ca^{2+}, i.e. strontium ions. This increases the final strength of the set cement (3,35,36). In Fuji IX and Equia, substitution of Ca with Sr accelerates matrix formation due to the lower ionization energy and higher reactivity of Sr. Additionally, the expansion of the glass network, attributed to the larger ionic radius of Sr compared with Ca, has been reported to promote apatite formation significantly. (37,38). Fluoride and strontium both have positive effects on remineralization progress, and when incorporated together, F and Sr improve apatite crystallinity and markedly reduce the acid reactivity (39). The leaching of ions from bioactive materials is beneficial because the ions interact with tissues; however, it can be associated with increased porosity and deterioration of mechanical properties over time (4), which explains the results of the present study. Indeed, a previous study showed that Fuji and Equia modifications with BAG2 and BAG1 resulted in greater F release (20), whereas the present study shows that despite a higher ZnO content, the microhardness was negatively affected by BAG2 incorporation (24).

When BAG is added to the original GIC structure, especially the one that is not highly reactive in the acid-base reaction (e.g. 45S5, which is not a source of Al^{3+}), it does not directly participate in the formation of the ionic network. Still, it behaves more like inert or passive filler in the initial stages. This reduces the proportion of highly reactive species. Hydration of powder particles in an acid-base reaction is less effective, which results in a lower crosslinking rate in the polysalt matrix. Since the matrix holds the partially reacted or unreacted glass particles together (whose portion may increase in modified materials), this may directly affect microhardness. This observation is closely related to the previous reports that the addition of BAGs caused preferential crosslinking by Ca^{2+} ions during setting, whereas Al^{3+} ions remained unreacted in the original cement powder or as free ions in the cement matrix (40,41). This finding suggests that Al release was controlled by surface reactions rather than by diffusion. (42).

Fuji and its modified variant, Fuji+BAG1, showed the highest microhardness values after 7 days, with no statisti-

rida (BAG1) nije značajno utjecala na mikrotvrdoću poslije 24 sata i poslije 7 dana. Suprotno tomu, modifikacija bioaktivnim staklom s višim udjelom fluorida (BAG2) značajno je smanjila mikrotvrdoću u oba materijala. Promatrajući mikrotvrdoću kroz vrijeme, porast je uočen u svim skupinama, a bio je statistički značajan u komercijalnim i eksperimentalnim formulacijama. Time su nulte hipoteze odbačene.

Iako su autori više studija uspoređivali mikrotvrdoću GIC materijala (31 – 33), ograničen je broj istraživanja u kojima su ispitivane promjene površinske mikrotvrdoće ovih materijala nakon modifikacije bioaktivnim staklom (34). Učinci modifikacija BAG1 i BAG2 na mikrotvrdoću GIC-a mogu se objasniti razlikama u sastavu materijala Fuji IX i Equia te utjecajem bioaktivnoga stakla na proces stvrdnjavanja. Naime, mehanizam stvrdnjavanja GIC-a uključuje hidrataciju čestica praha te umrežavanje karboksilnih skupina poliakrilne kiseline s otpuštenim ionima (Sr^{2+} i Al^{3+}), nakon čega nastaje silika-gel. Sporo pokretni ioni Al^{3+} ulaze u vodeni medij i umrežuju lance poliakrilne kiseline istiskujući Ca^{2+}, odnosno stroncijeve ione. To povećava konačnu čvrstoću očvrsloga cementa (3,35,36). U materijalima Fuji IX i Equia zamjena kalcija stroncijem ubrzava formiranje matrice zbog niže energije ionizacije i veće reaktivnosti stroncija. Dodatno, širenje staklene mreže, koje se pripisuje većem ionskom radijusu stroncija u usporedbi s kalcijem, značajno potiče stvaranje apatita (37, 38). Fluoridi i stroncij pozitivno djeluju na remineralizacijski proces, a kada su zajedno ugrađeni, željezo i stroncij poboljšavaju kristaliničnost apatita te značajno smanjuju kiselinsku reaktivnost (39). Otpuštanje iona iz bioaktivnih materijala korisno je zato što ti ioni stupaju u interakciju s tkivima, no može biti povezano s povećanom poroznošću i pogoršanjem mehaničkih svojstava tijekom vremena (4), što objašnjava rezultate ove studije. Doista, prethodno istraživanje pokazalo je da su modifikacije materijala Fuji i Equia s BAG-om 2 i BAG-om 1 izazvale povećano otpuštanje fluorida (20), a ova studija pokazuje da je mikrotvrdoća negativno pogođena ugradnjom BAG-a 2, unatoč višem sadržaju cinkova oksida (24).

Kada se BAG doda u izvornu strukturu GIC-a, osobito onoga koji nije visoko reaktivan u kiselinsko-baznoj reakciji (npr., 45S5, koji nije izvor Al^{3+}), on ne sudjeluje izravno u formiranju ionske mreže, nego se u početnim fazama ponaša više kao inertno ili pasivno punilo. Time se smanjuje udio visoko reaktivnih vrsta. Hidratacija čestica praha u kiselinsko-baznoj reakciji manje je učinkovita, što rezultira nižom brzinom umrežavanja u polisolnom matriksu. Budući da matriks drži zajedno djelomično reagirane ili nereagirane staklene čestice (čiji se udio može povećati u modificiranim materijalima), to može izravno utjecati na mikrotvrdoću. To opažanje usko je povezano s dosadašnjim istraživanjima u kojima se navodi da je dodatak BAG-a potaknuo preferencijalno umrežavanje Ca^{2+} ionima tijekom stvrdnjavanja, dok su Al^{3+} ioni ostali nevezani u izvornom prahu cementa ili kao slobodni ioni u cementnom matriksu (40, 41). Ti rezultati sugeriraju da je oslobađanje Al kontrolirano reakcijama na površini, a ne difuzijom (42).

Fuji i njegova modificirana varijanta, Fuji + BAG1, pokazali su najviše vrijednosti mikrotvrdoće poslije 7 dana,

cally significant difference between them. Also, Equia and Equia+BAG1 had comparable microhardness values after seven days. This result suggests that both Fuji and Equia have stable and strong ionic networks that can integrate 5 wt% bioactive particles without compromising mechanical properties, but with lower percentage of fluorides and ZnO. On the contrary, the interaction of BAG2 (whose composition differs significantly from the original Hench formulation) and the cement matrix could interfere with the setting process. In addition, it could negatively affect the cement's structural integrity, and initiate ion release (11). The study of Loh *et al.* (43) supports our results, claiming that VHN decreases with the higher concentration of CaF_2 in 45S5 based bioactive glass. That explains why BAG2 has an adverse effect on GIC materials. Additionally, Prabhakar *et al.* (34) found that modification with 10 wt % of bioactive glass S53P4 decreases the microhardness of conventional GIC. Our results are in line with the study of Abuzinadah *et al.* (20) where results showed that Fuji has greater microhardness values than Equia. Since microhardness reflects a material's resistance to wear and its behavior under load, it is crucial to note that Fuji IX formulations, with or without BAG, provide better initial mechanical stability. However, lower initial microhardness values are expected for Equia cement, given that this restorative system is designed to be applied with its own nano-filled coat. The coat was not used in this study. It has been shown that applying the coat significantly increases its mechanical properties (44). It is therefore not surprising that the microhardness values of Equia modifications are lower than Fuji modifications. Consequently, our study does not match with Moshaverinia *et al.* (45) and Bilge *et al.* (46). However, the primary purpose of this study was to test the impact of changes on each material.

The increased Zn content in experimental groups EF and FF did not yield the expected beneficial effect on microhardness. Our results are consistent with the findings of Zoergiebel et al. study (24) in which the positive effect of Zn on the mechanical behavior of ChemFil Rock was only partly confirmed: although improvement in flexural strength was recorded, microhardness and indentation modulus were reduced.

The results of the present study also show that the microhardness of all samples generally increases over time, which is consistent with the expected hardening and maturation of glass ionomer cement (2,47). An additional explanation can be given by ion release and mineralization due to the incorporation of the BAG particles (48). In opposition to that, Prabhakar et al. found the VHN of conventional GIC increased, while the modified GIC exhibited decreasing VHN over time. Zandi Karimi et al. (22) further demonstrated that adding 5 wt% of partially crystalline 45S5 BAG enhanced GIC's mechanical properties, and promoted mineralization within the matrix. Our findings follow a similar trend, with a pronounced increase after 7 days, likely due to ongoing ion exchange between BAG particles and the surrounding medium, thus contributing to cement maturation.

Finally, Dionysopoulos et al. (49) emphasized the importance of selecting optimal filler type and concentration. To-

bez statistički značajne razlike između njih. Također, Equia i Equia + BAG1 imale su usporedive vrijednosti mikrotvrdoće poslije sedam dana. Taj rezultat sugerira da i Fuji i Equia imaju stabilne i čvrste ionske mreže koje mogu integrirati 5 % masenoga udjela bioaktivnih čestica bez narušavanja mehaničkih svojstava, ali uz niži udio fluorida i cinkova oksida. Nasuprot tomu, interakcija BAG-a 2 (čiji se sastav značajno razlikuje od izvorne Henchove formulacije) s matriksom cementa može ometati proces stvrdnjavanja, negativno utjecati na strukturni integritet cementa te potaknuti otpuštanje iona (11). Studija Loha i suradnika (43) podupire naše rezultate – u tom se istraživanju navodi da se VHN smanjuje s većom koncentracijom kalcijeva fluorida (CaF_2) u 45S5 bioaktivnom staklu. To objašnjava zašto BAG2 nepovoljno utječe na GIC materijale. Dodatno, Prabhakar i suradnici (34) utvrdili su da modifikacija s 10 % masenoga udjela bioaktivnoga stakla S53P4 smanjuje mikrotvrdoću konvencionalnog GIC-a. Naši rezultati u skladu su sa studijom Abuzinadaha i suradnika (20) u kojoj je pokazano da Fuji ima veće vrijednosti mikrotvrdoće od materijala Equia. Budući da mikrotvrdoća odražava otpornost materijala na trošenje i njegovo ponašanje pod opterećenjem, važno je istaknuti da formulacije Fuji IX, s BAG-om ili bez BAG-a, pružaju bolju početnu mehaničku stabilnost. Međutim, niže početne vrijednosti mikrotvrdoće očekuju se za Equia cement, s obzirom na to da je taj restaurativni sustav predviđen za primjenu s vlastitim nanopunjenim premazom. U ovoj studiji premaz nije korišten. Primjena premaza dokazano značajno povećava njegova mehanička svojstva (44). Zato ne iznenađuje da su vrijednosti mikrotvrdoće modifikacija Equie niže od onih Fujijevih. Posljedično, naša studija nije u skladu s Moshaverinianom i suradnicima (45) i Bilgeaom i suradnicima (46). Međutim, primarni cilj ove studije bio je ispitati utjecaj modifikacija na svaki materijal.

Povećani sadržaj cinka u eksperimentalnim skupinama EF i FF nije rezultirao očekivanim pozitivnim učinkom na mikrotvrdoću. Naši rezultati u skladu su s nalazima istraživanja Zoergiebela i suradnika (24) u kojemu je pozitivan učinak cinka na mehaničko ponašanje materijala ChemFil Rock samo djelomično potvrđen: iako je zabilježeno poboljšanje čvrstoće na savijanje, bili su smanjeni mikrotvrdoća i modul indentacije.

Rezultati ove studije također pokazuju da se mikrotvrdoća svih uzoraka općenito povećava s vremenom, što je u skladu s očekivanim očvršćivanjem i dozrijevanjem staklenoionomernoga cementa (2, 47). Dodatno objašnjenje može se dati otpuštanjem iona i mineralizacijom zbog ugradnje čestica BAG-a (48). Suprotno tomu, Prabhakar i suradnici utvrdili su da se VHN konvencionalnoga GIC-a povećava, a kod modificiranoga tijekom vremena se smanjuje. Zandi Karimi i suradnici (22) također su pokazali da dodavanje 5 % masenoga udjela djelomično kristalnoga BAG-a 45S5 poboljšava mehanička svojstva GIC-a te potiče mineralizaciju unutar matriksa. Naši rezultati slijede sličan trend, s izraženim porastom poslije 7 dana, vjerojatno zbog kontinuirane ionske izmjene između čestica BAG-a i okolnog medija, što pridonosi dozrijevanju cementa.

gether with previously reported increased F and Ca ion release in materials modified with BAG1 and BAG2 (11), the 7-day microhardness results of the present study highlight the importance of balancing the concentration and type of BAG in order to optimize the combination of mechanical stability and bioactivity. Modification with BAG1 particles appears more suitable for Fuji and Equia, whereas the addition of BAG2 with higher Zn and F content resulted in a significant reduction in microhardness of both materials after 7 days.

The addition of bioactive glass particles could lead to the precipitation of calcium phosphates on the surface of BAG-modified GICs. Several *in vitro* studies have shown that the surface of GIC modified with bioactive glass particles forms apatite-like crystals when immersed in physiological fluids such as SBF (50–53). However, it was not confirmed in this study because a SEM-EDS analysis showed no hydroxyapatite-like crystals on the sample surface. Nevertheless, granular precipitates on the surface of most samples could be visualized, but probably because of the manipulation with the sample after the drying procedure, which rendered the sample fragile and prone to fragmentation. The assumption that the adhering particles were crushed fragments was supported by the fact that their composition was like the sample's overall composition.

An EDS analysis revealed characteristic elemental compositions for all investigated groups. The spectra of the commercial groups showed the presence of elements typical of conventional glass ionomer cement, including Si, Al, Sr, Na, F, and P. In contrast, specimens modified with bioactive glass exhibited additional calcium peaks, thus confirming successful incorporation of BAG into both cement matrices, which is also confirmed in the study of Kim et al. (54). The elemental patterns were consistent between Equia Forte and Fuji IX, indicating comparable behavior of both materials upon bioactive glass modification. This suggests that the bioactive glass additives exert a material-independent effect, reinforcing the applicability of this approach across different conventional glass ionomer systems. These findings may serve as a basis for future *in vivo* investigations and for assessing their clinical relevance.

To fully understand the long-term performance and application of these materials in permanent restorations, further research is needed; particularly within minimally invasive dental procedures.

Conclusions

This *in vitro* study contributes to the understanding of the effects of bioactive glass incorporation into GICs. The observed changes over time may be associated with the ongoing maturation of the cement matrix and potential interactions between the material components and the surrounding environment. However, the incorporation of bioactive glass did not induce *in vitro* bioactivity, as no hydroxyapatite-like crystal precipitation was observed on the material surfaces.

Konačno, Dionysopoulos i suradnici (49) istaknuli su važnost odabira optimalne vrste i koncentracije punila. Zajedno s već opisanim povećanim otpuštanjem željezovih i kalcijevih iona u materijalima modificiranima BAG-om 1 i BAG-om 2 (11), rezultati mikrotvrdoće poslije 7 dana u ovoj studiji ističu važnost ravnoteže koncentracije i vrste BAG-a kako bi se optimizirala kombinacija mehaničke stabilnosti i bioaktivnosti. Modifikacija s česticama BAG1 čini se prikladnijom za materijale Fuji i Equia, a dodatak BAG-a 2 s višim udjelom cinka i željeza znatno je smanjio mikrotvrdoću obaju materijala poslije 7 dana.

Dodatak čestica bioaktivnoga stakla može izazvati precipitaciju kalcijevih fosfata na površini BAG-modificiranih GIC-a. Nekoliko studija *in vitro* pokazalo je da GIC modificiran bioaktivnim staklom, kada je uronjen u fiziološke otopine poput SBF-a, na svojoj površini stvara kristale slične apatitu (50 – 53). No to u ovoj studiji nije potvrđeno zato što SEM-EDS analiza nije pokazala prisutnost hidroksiapatitu sličnih kristala na površini uzoraka. Ipak, na površini većine uzoraka mogli su se uočiti zrnati precipitati, ali to je vjerojatno posljedica rukovanja uzorkom nakon postupka sušenja, zbog čega je uzorak postao krhak i sklon pucanju. Pretpostavka da su prianjajuće čestice zapravo zdrobljeni fragmenti potkrijepljena je činjenicom da je njihov sastav bio sličan ukupnom sastavu uzorka.

EDS analiza otkrila je karakteristične elementarne sastave za sve ispitivane skupine. Spektri komercijalnih skupina pokazali su prisutnost elemenata tipičnih za konvencionalni staklenoionomerni cement, uključujući silicij, aluminij, stroncij, natrij, željezo i fosfor. Nasuprot tomu, uzorci modificirani bioaktivnim staklom pokazali su dodatne vrškove kalcija, što potvrđuje uspješnu inkorporaciju BAG-a u oba cementna matriksa, što je također potvrđeno u studiji Kima i suradnika (54). Elementarni obrasci bili su dosljedni između materijala Equia Forte i Fuji IX što upućuje na usporedivo ponašanje oba materijala pri modifikaciji bioaktivnim staklom. To sugerira da dodatci bioaktivnog stakla imaju učinak neovisan o materijalu, čime se potvrđuje primjenjivost ovog pristupa na različite konvencionalne staklenoionomerne sustave. Ti nalazi mogu poslužiti kao temelj za buduća istraživanja *in vivo* te za procjenu njihove kliničke relevantnosti. Potrebna su daljnja istraživanja kako bi se procijenila dugoročna učinkovitost tih materijala i njihov potencijal za primjenu u trajnim restauracijama, osobito u kontekstu minimalno invazivnih stomatoloških postupaka.

Zaključak

Ova *in vitro* studija pridonosi razumijevanju učinaka dodavanja bioaktivnog stakla u GIC materijale. Promjene koje su uočene tijekom vremena mogu se povezati s kontinuiranom sazrijevanjem cementa te mogućim interakcijama između sastavnih komponenti materijala i dodanih čestica. Međutim, inkorporacija bioaktivnog stakla nije potaknula bioaktivnost *in vitro* zato što na površinama materijala nije uočena precipitacija kristala sličnih hidroksiapatitu.

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Sažetak

Cilj rada: Svrha ove studije in *vitro* bila je procijeniti učinak bioaktivnih stakala koja sadržavaju manji udio fluora i cinka u nižem (BAG1) i višem omjeru (BAG2) na Vickersovu mikrotvrdoću (VHN), površinsku morfologiju i kemijski sastav visokoviskoznoga staklenoionomernoga i staklohibridnoga cementa. **Materijali i metode:** Fuji IX (Fuji) i EQUIA Forte HT (Equia) modificirani su s 5 posto masenih postotaka (5 wt%) BAG1 i BAG2. Pripremljeno je šest skupina koje su pohranjene u destiliranoj vodi: Fuji, Fuji + BAG1, Fuji + BAG2, Equia, Equia + BAG1 i Equia + BAG2. BAG1 i BAG2 analizirani su FTIR-om. VHN je izmjeren poslije 24 sata i poslije 7 dana. Reprezentativni uzorci iz svih skupina pohranjeni su u puferiranoj otopini fosfata i analizirani s pomoću SEM-EDS-a. Podatci su analizirani ANOVA-om i uparenim t-testom ($\alpha = 0,05$). **Rezultati:** Fuji i Fuji + BAG1 pokazali su najvišu vrijednost VHN-a u oba razdoblja mjerenja, a u skupini BAG2 značajno se smanjila mikrotvrdoća u usporedbi s izvornim materijalima Fuji i Equia ($p < 0,05$). Sve su skupine pokazale porast VHN-a tijekom 7 dana ($p < 0,05$). FTIR je potvrdio amorfni silikatni i fluoridni sadržaj. SEM-EDS potvrdio je izostanak kristalnih precipitata na površini materijala pri skladištenju u otopini koja sadrži fosfat. **Zaključak:** BAG1 očuvao je ili blago povećao mikrotvrdoću, a BAG2 značajno ju je smanjio. Na izvornim materijalima, ni na materijalima modificiranima s 5 masenih postotaka (5 wt%) bioaktivnog stakla, nisu uočeni kristalni precipitati. Optimizacija sastava BAG-a ključna je za postizanje ravnoteže između mehaničke stabilnosti i bioaktivnosti skalenoionomernih cemenata.

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Adresa za dopisivanje
Ivan Šalinović
Sveučilište u Zagrebu, Stomatološki fakultet
Zavod za endodonciju i restaurativnu stomatologiju
Gundulićeva 5, 10 000 Zagreb, Hrvatska
telefon: +38514802126
isalinovic@sfzg.unizg.hr

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