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Mjerenje temperature u stvarnom vremenu tijekom svjetlosno aktivirane polimerizacije eksperimentalnih kompozitnih materijala

Real-time Temperature Monitoring During Light-Curing of Experimental Composites

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Sažetak

Cilj: Željelo se ispitati porast temperature u stvarnom vremenu tijekom svjetlosno aktivirane polimerizacije eksperimentalnih kompozitnih materijala koji sadržavaju bioaktivno staklo 45S5 (BG) i usporediti ga s porastom temperature triju komercijalnih kompozitnih materijala. **Materijali i metode:** Pripremljeno je pet eksperimentalnih kompozitnih materijala s ukupnim težinskim udjelom punila od 70 % i težinskim udjelima BG-a između 0 i 40 %. Cilindrični uzorci promjera 6 mm i debljine 2 mm osvijetljeni su 30 sekunda polimerizacijskim uređajem Bluephase G2 (Ivoclar Vivadent) pri 1200 mW/cm². Porast temperature tijekom svjetlosne aktivacije polimerizacije mjeren je na dnu uzoraka termočlanom T-tipa, uz brzinu prikupljanja podataka od 20 sekunda¹. Kako bi se izmjerio doprinos zagrijavanja polimerizacijskog uređaja, polimerizirani uzorci ostavljeni su da se ohlade na sobnu temperaturu, nakon čega su naknadno osvijetljeni (30 s). Statistička analiza obavljena je jednosmjernom analizom varijance (ANOVA) i Pearsonovom analizom korelacija, uz razinu značajnosti $\alpha = 0,05$. **Rezultati:** Vrijednosti temperature izmjerene tijekom svjetlosno aktivirane polimerizacije eksperimentalnih kompozita bile su između 12,2 i 14,0 °C, što se može usporediti s vrijednostima tekućega komercijalnog kompozita (12,5 °C), ali više od vrijednosti izmjerenih za nano- i mikrohibridne komercijalne kompozite (9,6–10,3 °C). Porast temperature tijekom naknadnog osvijetljivanja bio je sličan u svim kompozitima (7,8–9,1 °C). Za eksperimentalne kompozite porast temperature, zbog egzotermne reakcije, iznosio je 3,1–5,8 °C i negativno je korelirao s težinskim udjelom BG-a ($R^2 = 0,94$). Temperaturni porast dosegnute maksimalne vrijednosti za 6,5 do 19,8 sekunda nakon početka osvijetljivanja, a vremena pri kojima su dosegnute maksimalne vrijednosti pozitivno su korelirala s težinskim udjelom BG-a ($R^2 = 0,98$). **Zaključak:** Porast temperature zbog svjetlosno aktivirane polimerizacije eksperimentalnih kompozitnih materijala može se usporediti s porastom temperature komercijalnih kompozita. Zato se količina oslobođene topline može smatrati sigurnom za zubnu pulpu.

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Uvod

Suvremeni kompozitni materijali za izravne restauracije omogućuju izvrsnu estetiku uz prihvatljiva mehanička svojstva (1). Trajnost kompozitnih restauracija skraćena je zbog njihove sklonosti prema razvoju sekundarnog karijesa (2). Kako bi se to spriječilo, istražuju se bioaktivni kompozitni materijali koji imaju antibakterijska svojstva ili otpuštaju remineralizirajuće ione (3). Različite bioaktivne formulacije pokazale su obećavajuće rezultate (3–7).

Između različitih spojeva koji otpuštaju ione i zato se istražuju kao potencijalna bioaktivna punila eksperimental-

Introduction

Modern composite materials for direct restorations offer excellent esthetics and reasonable mechanical properties (1). However, the durability of composite restorations is reduced by their susceptibility to development of secondary caries (2). The issue of secondary caries is being addressed by investigations of bioactive composites with the capability to combat cariogenic bacteria or release remineralizing ions (3). Various experimental bioactive formulations have been investigated with promising results (3-7).

Among different ion-releasing compounds which are be-

nih materijala, bioaktivno staklo (BG) višestruko korisno djeluje – brtvi marginalne pukotine precipitatom hidroksiapatita (5), remineralizira tvrda zubna tkiva (8), smanjuje dentinsku preosjetljivost i postoperativnu osjetljivost (9) te ima antibakterijski učinak (10). Svojstva BG-a, poput ravnoteže između stabilnosti i topljivosti u vodenom okolišu, određena su njegovim sastavom (11). Različite vrste BG-a bile su uključene u sastav eksperimentalnih dentalnih kompozita, primjerice niobijem modificirani BG (12), BG koji sadržava fluoride (13), BG sastava S53P4 (14) i BG sastava 45S5 (15). Klasična formulacija BG-a 45S5 slična je originalnom sastavu BG-a koji se na tržištu nalazi pod komercijalnim nazivom *Bioglass* i ima široku uporabu u ortopediji (16). Formulacija BG-a 45S5 sljedećeg je sastava (težinski udjeli): 45 % SiO_2 , 25 % Na_2O , 25 % CaO i 5 % P_2O_5 (17). Preliminarna istraživanja dentalnih kompozita punjenih BG-om 45S5 pokazala su povoljna svojstva poput stupnja konverzije (18), dubine polimerizacije (19), precipitacije hidroksiapatita (20) te apsorpcije vode i solubilnosti (21).

Stvrdnjavanje kompozitnih materijala može štetno utjecati na zubnu pulpu zbog porasta temperature tijekom svjetlosno aktivirane polimerizacije (22). Dva glavna izvora zagrijavanja su osvjetljavanje polimerizacijskim uređajem i egzotermna polimerizacija smolaste komponente (23). Uporaba suvremenih polimerizacijskih uređaja visokoga intenziteta (1000 mW/cm^2 i više) pridonosi porastu temperature putem obaju mehanizama: izravnim zagrijavanjem te ubrzanjem reakcije polimerizacije (24). Prema suvremenim smjernicama, uporaba polimerizacijskih uređaja visokog intenziteta smatra se sigurnom za zubnu pulpu pod uvjetom da se poštuju upute proizvođača o trajanju osvjetljavanja (25).

Cilj ovog istraživanja bio je ispitati porast temperature u stvarnom vremenu tijekom svjetlosne aktivacije polimerizacije pet eksperimentalnih kompozitnih materijala s različitim udjelima BG-a 45S5 (0 – 40 % težinski) i usporediti ga s porastom temperature pri polimerizaciji triju komercijalnih kompozita. Nulte hipoteze su sljedeće: (I) udjel BG-a ne utječe na porast temperature tijekom svjetlosne aktivacije polimerizacije eksperimentalnih kompozita; (II) udjel BG-a ne utječe na vrijeme potrebno sa se postigne najviša vrijednost temperature; (III) eksperimentalni materijali ne razlikuju se prema porastu temperature od komercijalnih referentnih materijala.

Materijali i metode

Kompozitni materijali

Sastav pet eksperimentalnih kompozita određen je preliminarnim istraživanjima (18 – 20) i detaljno prikazan u tablici 1. Smole i komponente sustava fotoinicijatora miješane su 48 sati u mraku magnetskom miješalicom. Dobivena fotoaktivirana smola pomiješana je s punilima u uređaju Speed Mixer TM DAC 150 FVZ (Hauschild & Co. KG, Hamm, Njemačka) pri 2700 okretaja u minuti, tijekom pet minuta (26). Paste eksperimentalnih kompozita zatim su 12 sati pohranjene u vakuumu kako bi se uklonile inkluzije zraka.

Uz eksperimentalne kompozite, tri komercijalna kompozita (tekući, nano- i mikrohibridni) ispitani su kao referen-

ing investigated as bioactive fillers in experimental materials, bioactive glass (BG) offers multiple potential benefits, such as sealing of the interfacial gap with hydroxyapatite precipitate (5), remineralization of demineralized dental hard tissues (8), reduction of dentin hypersensitivity and postoperative sensitivity (9) and antibacterial action (10). The properties of BG such as the balance between stability and solubility in an aqueous environment are determined by the BG composition (11). Various types of BG have been incorporated into dental materials, e.g. Nb-modified BG (12), fluoride-containing BG (13), BG S53P4 (14), and BG 45S5 (15). The “classical” BG 45S5 used in this study resembled the original BG formulation which is marketed under the commercial name of “Bioglass” and has a widespread use in orthopedics (16). The BG 45S5 comprises (in wt%): 45% SiO_2 , 25% Na_2O , 25% CaO , and 5% P_2O_5 (17). Preliminary studies on dental composites filled with BG45S5 have shown favorable properties such as the degree of conversion (18), depth of cure (19), the capability to precipitate hydroxyapatite (20), water sorption and solubility (21).

The setting of composite materials exerts a potentially harmful effect on the dental pulp due to the increase in temperature during light-curing (22). Two main sources of heat are irradiation from the light-curing unit and exothermic polymerization of the resinous component (23). The use of contemporary high-irradiance curing units (1000 mW/cm^2 and more) contributes to temperature increase through both the direct heating effect and by accelerating the polymerization reaction (24). However, curing of dental composites using high-irradiance curing units has been considered safe for dental pulp if curing times recommended by manufacturers are followed (25).

The aim of this study was to investigate the real-time temperature rise during light-curing of five experimental composite materials containing different fractions (0-40 wt %) of BG 45S5 and compare it to the temperature rise of three commercial composites. The null hypotheses were that: (I) the fraction of BG does not affect the temperature rise during light-curing of experimental composites; (II) the fraction of BG does not affect the time at which temperature reaches the maximum value; (III) the temperature rise in experimental bioactive composites does not differ from that in commercial reference materials.

Materials and methods

Composite materials

The composition of five experimental composite materials according to preliminary studies (18-20) is detailed in Table 1. Resins and photoinitiator system were mixed in a dark room using a magnetic stirrer for 48 hours. Blending of the resulting photoactivated resin with fillers was performed in a mixing device (Speed Mixer TM DAC 150 FVZ, Hauschild & Co. KG, Hamm, Germany) at 2700 rpm during five minutes (26). The experimental composite pastes were then kept for 12 h in vacuum to remove air inclusion.

Apart from the experimental composites, three commercial composites (flowable, nano- and micro-hybrid) were

tni materijali (tablica 2.). Informacije o sastavu komercijalnih materijala prikupljene su iz proizvođačkih brošura i referencija (27, 28).

used as a reference (Table 2). Information on the composition of commercial materials was obtained from manufacturer provided datasheets and references (27, 28).

Tablica 1. Sastav eksperimentalnih kompozitnih materijala
Table 1 Composition of experimental composites

Materijal • Material	Sastav punila (težinski %) • Filler composition (wt%)		Ukupni udio punila (wt%) • Total filler ratio (wt%)	Smola • Resin		Volumni udio punila (%) • Filler load (vol%)
	Bioaktivno staklo • Bioactive glass	Ojačavajuća punila • Reinforcing fillers (Ba:Si = 2:1)		Težinski udio (%) • wt%	Sastav • Composition	
BG-0	0	70	70	30	60 % Bis-GMA 40 % TEGDMA fotoinicijator • photoinitiator system: 0.2 % CQ 0.8 % 4E	48
BG-5	5	65	70	30		48
BG-10	10	60	70	30		48
BG-20	20	50	70	30		51
BG-40	40	30	70	30		52

Bioaktivno staklo: SiO₂ 45 %, Na₂O 25 %, CaO 25 %, P₂O₅ 5 %, veličina čestica (d50/d99 [μm]): 4.0/13.0, silanizacija: ne, naziv proizvoda/proizvođač: G018-144/Schott, Njemačka

Barijevo staklo (Ba): SiO₂ 55.0 %, BaO 25.0 %, B₂O₃ 10.0 %, Al₂O₃ 10.0 %, veličina čestica (d50/d99 [μm]): 1.0/4.0, silanizacija 3.2 wt %, naziv proizvoda/proizvođač: GM27884/Schott, Njemačka

Silika punila (Si): SiO₂ ≥ 99.8 %, veličina primarnih čestica: 12 nm, silanizacija 4-6 wt %, naziv proizvoda/proizvođač: Aerosil DT/Evonik Degussa, Njemačka

Bis-GMA: bisfenol-A glicidil metakrilat, Esstech, PA, SAD; TEGDMA: trietilen glikol dimetakrilat, Esstech; CQ: kamforkinon, Aldrich, WI, SAD; 4E: etil-4- (dimetilamino) benzoat, Aldrich

Bioactive glass: SiO₂ 45%, Na₂O 25%, CaO 25%, P₂O₅ 5%, particle size (d50/d99 [μm]): 4.0/13.0, silanization: none, product name/manufacturer: G018-144/Schott, Germany.

Barium-fillers (Ba): SiO₂ 55.0%, BaO 25.0%, B₂O₃ 10.0%, Al₂O₃ 10.0%, particle size (d50/d99 [μm]): 1.0/4.0, silanization 3.2 wt%, product name/manufacturer: GM27884/Schott, Germany.

Silica-fillers (Si): SiO₂ ≥ 99.8%, primary particle size: 12 nm, silanization 4-6 wt%, product name/manufacturer: Aerosil DT/Evonik Degussa, Germany.

Bis-GMA: Bisphenol A glycidyl methacrylate, Esstech, PA, USA; TEGDMA: tri-ethylene glycol dimethacrylate, Esstech; CQ: camphorquinone, Aldrich, WI, USA; 4E: ethyl-4- (dimethylamino) benzoate, Aldrich.

Tablica 2. Sastav komercijalnih kompozita
Table 2 Composition of commercial composites

Materijal (kratica) • Material (abbreviation)	Proizvođač • Manufacturer	Nijansa / LOT / EXP • Shade / LOT / EXP	Sastav punila • Filler composition	Udio punila (težinski / volumni) • Filler ratio (wt% / vol%)	Smola • Resin
Tetric EvoFlow (TEF)	Ivoclar Vivadent, Schaan, Lihtenštajn • Liechtenstein	A2 / V36426 / 2020-09-02	Barijevo staklo, iterbijev trifluorid, miješani oksidi, visoko raspršena silika, prepolymeri • Barium glass, ytterbium trifluoride, mixed oxide, highly dispersed silica, prepolymers	65 / 40	Bis-GMA, UDMA, dekandioldimetakrilat • decandioldimethacrylate
Tetric EvoCeram (TEC)	Ivoclar Vivadent, Schaan, Lihtenštajn • Liechtenstein	A2 / V40834 / 2020-10-13	Barijevo staklo, iterbijev trifluorid, miješani oksidi, prepolymeri • Barium glass, ytterbium trifluoride, mixed oxide, prepolymers	76 / 54	Bis-GMA, UDMA, Bis-EMA
Gradia Direct Posterior (Gradia)	GC Europe, Leuven, Belgija • Belgium	A3 / 1503202 / 2018-03	Barijevo staklo, silika, prepolymeri • Barium glass, silica, prepolymers	77 / 65	UDMA, dimetakrilati • dimethacrylates

Bis-EMA: ethoxylated bisphenol A dimethacrylate, UDMA: urethane dimethacrylate •

Bis-EMA: etoksilirani bisfenol-A dimetakrilat, UDMA: uretan dimetakrilat

Mjerenje temperature u stvarnom vremenu

Za mjerenje porasta temperature tijekom svjetlosno aktivirane polimerizacije pripremljeni su cilindrični uzorci promjera 6 mm i debljine 2 mm u crnim teflonskim kalupima. Nepolimerizirani materijal postavljen je u kalup koji je zatim s objiju strana pokriven polietilen-tereftalatnim (PET) filmom

Real-time temperature monitoring

To measure the temperature rise during light-curing, cylindrical composite specimens of 6 mm in diameter and 2 mm thick were prepared in black Teflon molds. The uncured composite material was cast into molds and covered from both sides with 0.05 mm thick polyethylene terephthalate

debljine 0,05 mm. Kalupi ispunjeni kompozitnim materijalom nakon toga pokriveni su s obje strane staklenim pločicama debljine 1 mm i pritisnuti između metalnih utega ravne površine kako bi se uklonio suvišak materijala. Termočlanak T-tipa smješten je na suprotnoj strani uzorka ispod PET filma. Preliminarna mjerenja pokazala su da postavljanje PET filma između kompozitnog uzorka i termočlanaka nema značajan učinak na temperaturne krivulje, nego samo neznatno pridonosi nasumičnoj pogrešci mjerenja. Detaljni opis eksperimentalnog postava dostupan je u referenciji (23). Šest uzoraka pripremljeno je za svaki kompozitni materijal ($n = 6$).

Tijekom svjetlosno aktivirane polimerizacije (30 s) uređajem Bluephase G2 (Ivoclar-Vivadent, Schaan, Lihtenštajn) s plavo-ljubičastom svjetlećom diodom (LED) intenziteta 1200 mW/cm^2 , temperatura uzoraka mjerena je u stvarnom vremenu (20 s^{-1}) s pomoću računalnog programa vlastite izrade pripremljenog u paketu LabVIEW 2011 (National Instruments, Austin, Texas, SAD). Mjerenje temperature nastavljeno je i nakon što je ciklus osvjetljivanja završen kako bi se pratilo hlađenje uzorka. Približno 160 sekunda nakon početka svjetlosno aktivirane polimerizacije, temperatura se spustila na početnu vrijednost. Zatim je uzorak osvjetljen još jedanput i to 30 sekunda. Takav postupak omogućio je odvajanje učinaka zagrijavanja polimerizacijskim uređajem od egzotermne reakcije polimerizacije. Opisani pristup pretpostavlja da je polimerizacija završena tijekom prvog osvjetljivanja, što je potvrđeno preliminarnim pokusima. Temperatura okoliša izmjerena T-tipom termočlanaka kao vrijednost zabilježena prije početka mjerenja u stvarnom vremenu, iznosila je $21 \pm 1 \text{ }^\circ\text{C}$.

Statistička analiza

Normalnost distribucije i prihvatljiva homogenost varijanci potvrđene su Shapiro-Wilkovim i Leveneovim testom. Jednosmjernom ANOVA-om s Tukeyjevom post-hoc prilagodnom uspoređene su srednje vrijednosti temperaturnog porasta svih kompozita s vremenom vršnih vrijednosti temperature u eksperimentalnim kompozitima. Pearsonovom analizom koreliran je težinski udjel BG-a s toplinom oslobođenom u egzotermnoj reakciji i vremenom postizanja temperaturnog maksimuma. Statistička analiza obavljena je u programskom paketu SPSS 20 (IBM, Armonk, NY, SAD), uz $\alpha = 0,05$.

Rezultati

Reprezentativna krivulja porasta temperature kao funkcije vremena prikazana je na slici 1. Porast temperature pri prvom osvjetljivanju ukupni je porast temperature tijekom svjetlosno aktivirane polimerizacije (T_1), a porast temperature pri drugom osvjetljivanju odražava učinak zagrijavanja polimerizacijskim uređajem (T_2). Razlika između T_1 i T_2 pokazuje porast temperature koji se može pripisati energiji oslobođenoj u egzotermnoj polimerizaciji (T_{exotherm}).

Srednje vrijednosti T_1 , T_2 i T_{exotherm} prikazane su na slici 2. Porast temperature zbog zagrijavanja polimerizacijskim uređajem (T_2) bio je sličan u svim kompozitima. Kad je riječ

(PET) film. The composite-filled molds were covered from both sides with 1 mm thick glass plates and pressed between two flat metal slabs to remove excess material. The curing unit was centered above the specimen at the distance of 1 mm from its surface. A custom-made t-type thermocouple was positioned at the opposite side of the specimen below the PET film. Preliminary measurements showed that placing the PET film between the composite specimen and thermocouple had no significant effect on real-time temperature curves, rather adding only slightly to the random measurement error. The detailed description of the experimental setup is given in the reference (23). Six specimens were prepared for each composite material ($n=6$).

During the light-curing for 30 s by means of a blue-violet light emitting diode (LED) curing unit (Bluephase G2, Ivoclar-Vivadent, Schaan, Liechtenstein, irradiance of 1200 mW/cm^2), the temperature of the specimens was monitored in real-time (20 s^{-1}) using a custom-made computer program prepared in LabVIEW 2011 (National Instruments, Austin, Texas, USA). Temperature monitoring was continued after the curing has been completed in order to observe the specimen cooling. Approximately 160 seconds after the start of the curing, temperature returned to the baseline and the specimen was illuminated again for 30 seconds. This procedure was performed in order to discern the heating effect of the curing unit from the polymerization exotherm. Such an approach assumes that polymerization has been completed during the first illumination, which was demonstrated in preliminary experiments. The environmental temperature recorded using a t-type thermocouple as the baseline temperature before initiating the real-time temperature measurement was $21 \pm 1 \text{ }^\circ\text{C}$.

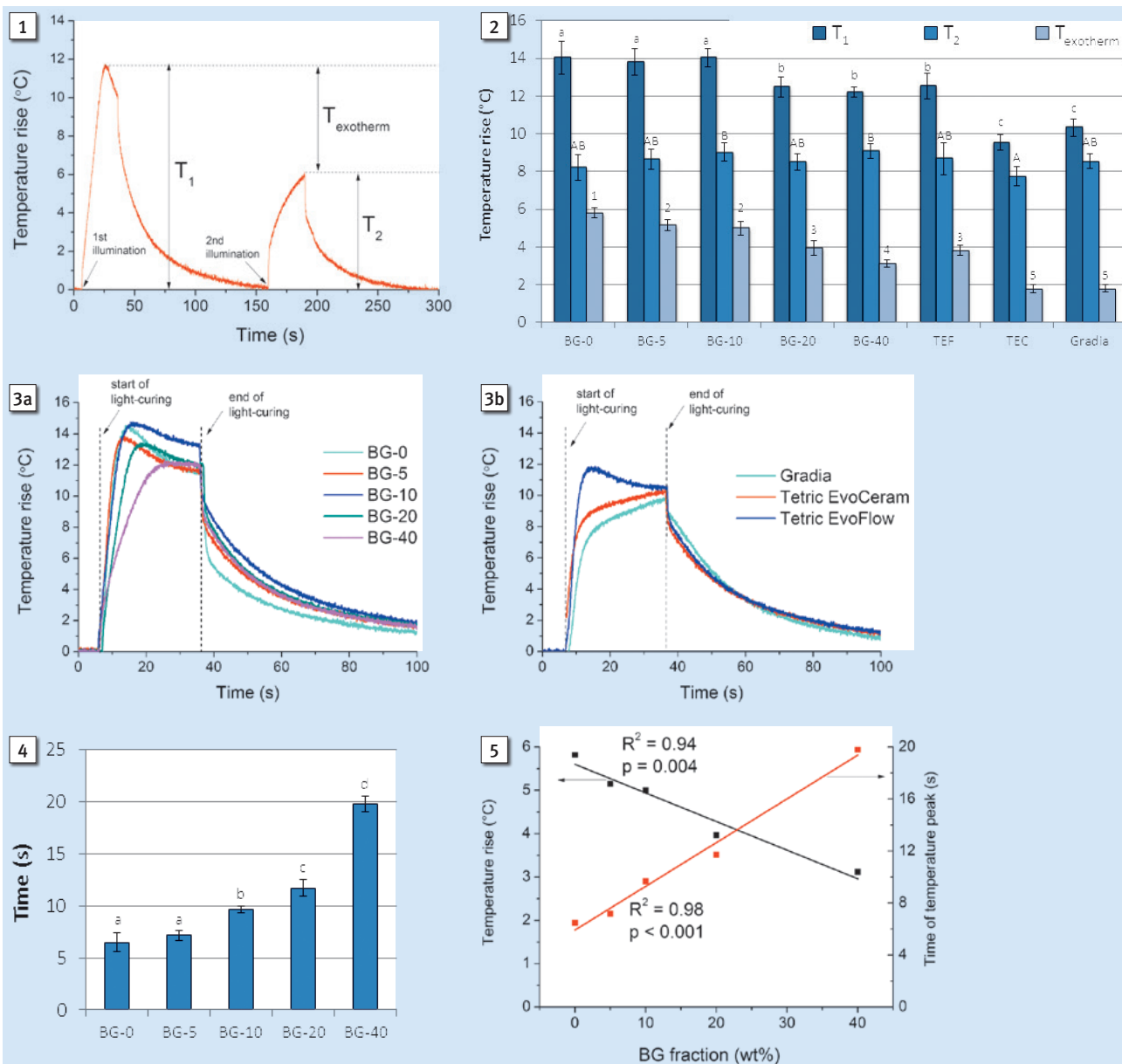
Statistical analysis

No significant deviations from a normal distribution and an acceptable homogeneity of variances were confirmed by the Shapiro Wilk and Levene's test, respectively. The one-way ANOVA with Tukey post-hoc adjustment was used to compare mean values of temperature rise among all composites, as well as times of the temperature peak among the experimental composites. A Pearson correlation analysis was performed to correlate the BG fraction with the reaction exotherm and time of the temperature peak. Statistical analysis was performed in SPSS 20 (IBM, Armonk, NY, USA) with $\alpha=0.05$.

Results

A representative plot of the temperature increase as a function of time is presented in Figure 1. The temperature rise during the first illumination represents the total temperature rise during light-curing (T_1), while the temperature rise during the second illumination reflects the heating effect of the curing unit (T_2). The difference between T_1 and T_2 represents the temperature rise due to the polymerization exotherm (T_{exotherm}).

Mean values of T_1 , T_2 , and T_{exotherm} are presented in Figure 2. The temperature rise due to the curing unit heating (T_2) was similar for all composites. T_1 values for BG-20 and BG-



Slika 1. Reprezentativna krivulja porasta temperature u stvarnom vremenu (materijal: TEF); vršna vrijednost temperature tijekom prvog osvjetljavanja (T_1) označava porast temperature tijekom svjetlosne aktivacije polimerizacije i zbroj je učinaka zagrijavanja i egzotermne reakcije; druga vršna vrijednost (T_2) uzrokovana je zagrijavanjem polimerizacijskim uređajem; razlika između navedenih parametara pokazuje porast temperature koji se može pripisati oslobađanju energije u polimerizacijskoj reakciji (T_{exotherm})

Figure 1 Representative plot of the real-time temperature rise (material: TEF). The temperature peak during the first illumination (T_1) represents the temperature increase during light curing, which is a sum of the heating effect from the curing unit and the reaction exotherm. The second peak (T_2) is solely due to the curing unit heating. The difference between these two values represents the temperature rise which is attributable to the exotherm of the polymerization reaction (T_{exotherm}).

Slika 2. Srednje vrijednosti (\pm s.d.) temperaturnog porasta tijekom svjetlosne aktivacije polimerizacije (T_1), tijekom naknadnog osvjetljavanja (T_2) i egzotermne reakcije (T_{exotherm}); statistički homogene skupine označene su istim malim slovima za T_1 , istim velikim slovima za T_2 i istim brojevima za T_{exotherm}

Figure 2 Mean values (\pm s.d.) of temperature rise during light curing (T_1), during additional illumination (T_2) and polymerization exotherm (T_{exotherm}). Statistically homogeneous groups are denoted with same lowercase letters for T_1 , same uppercase letters for T_2 , and same numbers for T_{exotherm} .

Slika 3. Povećani prikaz početnog dijela temperaturnih krivulja (tijekom prvog osvjetljavanja) u eksperimentalnim kompozitima (a) i komercijalnim referentnim materijalima (b)

Figure 3 A close-up of the initial part of temperature curves (during the first illumination) for experimental composites (a) and commercial reference composites (b).

Slika 4. Vrijeme postizanja vršne vrijednosti temperature (srednje vrijednosti \pm s.d.) u eksperimentalnim kompozitima; statistički homogene skupine označene su istim malim slovima

Figure 4 Time of the temperature peak (mean values \pm s.d.) for experimental composites. Statistically homogeneous groups are denoted with same lowercase letters.

Slika 5. Porast temperature i vrijeme vršne vrijednosti temperature kao funkcija težinskog udjela BG-a; opažene su visoko značajne korelacije s visokim koeficijentima determinacije

Figure 5 Temperature rise and the time of temperature peak plotted as a function of the BG fraction. Highly significant correlations with high coefficients of determination were observed.

o BG-20 i BG-40, izmjerene vrijednosti T_1 značajno su niže negoli u eksperimentalnim kompozitima s nižim udjelima BG-a. Vrijednosti T_{exotherm} imale su veću diskriminatornu snagu s obzirom na udjel BG-a, pokazujući postupni pad s povećanjem udjela BG-a. Za tekući komercijalni referentni materijal (TEF) izmjerene su vrijednosti T_1 i T_{exotherm} slične onima za BG-20, a T_1 i T_{exotherm} u nano- i mikrohibridnim komercijalnim kompozitima (TEC i Gradia) bili su niži negoli u eksperimentalnim kompozitima.

Slika 3. pokazuje temperaturne krivulje tijekom prvog osvjetljivanja eksperimentalnih kompozita (a) i komercijalnih referentnih materijala (b). U eksperimentalnim kompozitima je povećanje težinskog udjela --a utjecalo na snižavanje vršne vrijednosti temperature i njezino pomicanje prema kasnijim vremenima (slika 3.a). U komercijalnim kompozitima vršna vrijednost temperature uočena je samo pri uporabi TEF-a, a za materijale TEC i Gradia zabilježen je postupni porast temperature prema kraju osvjetljivanja (slika 3. b). Srednje vrijednosti vremena pri kojima je postignut temperaturni maksimum u eksperimentalnim kompozitima prikazane su na slici 4. Uočen je statistički značajan učinak udjela BG-a na vrijeme temperaturnog maksimuma.

Slika 5. pokazuje porast temperature i vrijeme temperaturnog maksimuma kao funkciju težinskoga udjela BG-a. Ustanovljene su visoke korelacije udjela BG-a s vremenom temperaturnog maksimuma ($R^2 = 0,98$) i porastom temperature ($R^2 = 0,94$).

Rasprava

U ovom istraživanju ispitan je porast temperature u stvarnom vremenu tijekom svjetlosno aktivirane polimerizacije eksperimentalnih kompozita s težinskim udjelom BG-a od 0 do 40 % i ukupnim težinskim udjelom punila od 70 %. Tri komercijalna kompozita (tekući, nano- i mikrohibridni) služili su kao referencije.

Sastav eksperimentalnih kompozita utvrđen je u ranijem istraživanju koje je potvrdilo njihovo svojstvo da precipitiraju hidroksiapatit (20). Taj potencijal rastao je s porastom težinskog udjela BG-a. Istodobno može se očekivati da će povećanje udjela topljivog BG-a negativno djelovati na mehanička svojstva (29). Ispitani su eksperimentalni kompoziti s različitim udjelima BG-a, s obzirom na to da još nije određen optimalni sastav koji bi osigurao uravnoteženu bioaktivnost i mehaničku stabilnost (21).

Uzorcima debljine 2 mm simulirana je debljina sloja koja je uobičajena pri kliničkoj uporabi konvencionalnih kompozita. Budući da količina oslobođene topline ovisi o količini kompozita (22), dimenzije kompozitnih uzoraka odabrane su tako da prikazuju volumen materijala koji je potreban za izradu velikog sloja pri oblikovanju ispuna u opsežnoj preparaciji na stražnjim zubima. Vrijeme svjetlosne aktivacije polimerizacije od 30 sekunda premašuje uobičajene preporuke koje su za polimerizacijske uređaje visokog intenziteta (1200 mW/cm^2) najčešće između 10 i 20 sekunda. Produživanjem osvjetljivanja dobiven je bolji uvid u temperaturne krivulje i uočena je vršna vrijednost temperature za sve eksperimentalne materijale (slika 3.).

40 were significantly lower than those for composites with lower BG fractions. The T_{exotherm} values were statistically more discriminative regarding the BG fraction and showed a gradual decline as the BG fraction increased. The flowable commercial reference (TEF) showed T_1 and T_{exotherm} values similar to those of BG-20, while T_1 and T_{exotherm} for the nano- and micro-hybrid commercial references (TEC and Gradia) were lower than in experimental composites.

Figure 3 shows temperature curves during the first illumination for experimental composites (a) and commercial references (b). In experimental composites, the temperature peak became lower and shifted towards later times as the BG fraction increased (Figure 3a). In commercial composites, the temperature peak was observed only in TEF, while TEC and Gradia showed a gradual temperature increase until the end of the illumination (Figure 3b). The time at which temperature maximum in experimental composites was reached is summarized in Figure 4. Statistically significant influence of the BG fraction on the time of temperature peak was observed.

Figure 5 plots temperature rise and time of temperature peak as a function of the BG fraction. High correlations with BG fraction were identified for the time of the temperature peak and temperature rise (R^2 values of 0.98 and 0.94, respectively).

Discussion

This study assessed the real-time temperature rise during light-curing of experimental composites filled with 0-40 wt% of BG 45S5 and total filler loading of 70 wt%. Three commercial composites (flowable, nano- and micro-hybrid) were used as references.

The composition of experimental composites followed a previous study which demonstrated their capability to precipitate hydroxyapatite (20). The potential for hydroxyapatite precipitation was increased with higher BG fractions. However, increasing the fraction of water-soluble BG fillers is expected to impair mechanical properties (29). Thus composites with various BG fractions were investigated since the optimal composition which would provide a balance between bioactivity and mechanical stability has not yet been determined (21).

The thickness of the specimens used in this study was 2 mm in order to simulate the layer thickness which is common in the clinical use of conventional composites. Since the amount of heat released depends on the composite amount (22), the dimensions of composite specimens were chosen to represent the volume of the composite which would be used in a large increment for filling an extensive preparation in posterior teeth. The curing time of 30 seconds exceeds the commonly recommended curing times, which usually range between 10 and 20 seconds for a high-irradiance curing unit with an output of 1200 mW/cm^2 . Such a long curing time was used in order to gain a better insight into temperature curves during polymerization and capture the temperature peaks for all experimental materials (Figure 3).

Pristup koji uključuje dva uzastopna osvjetljivanja (slika 1.) prihvaćen je nastavno na ranije istraživanje u kojem se pokazao korisnim za odvajanje toplinskih doprinosa podrijetlom od polimerizacijskog uređaja i egzotermne reakcije polimerizacije (23). Statistička analiza pokazala je da se razlike u temperaturnom porastu između materijala najvećim dijelom mogu pripisati egzotermnoj reakciji, a učinak zagrijavanja polimerizacijskim uređajem bio je sličan za sve materijale, s obzirom na to da svi imaju sličan toplinski kapacitet (slika 2.). Zato padajući trend temperaturnih porasta tijekom svjetlosno aktivirane polimerizacije (T_1) zapravo odražava sličan uzorak opažen za T_{exotherm} . Razlike u težinskim udjelima BG-a rezultirale su s više statistički značajnih razlika u parametru T_{exotherm} negoli u T_1 , što se može objasniti manjom varijabilnošću podataka u slučaju prvog parametra. U svakom slučaju može se uočiti statistički značajan učinak težinskog udjela BG-a na porast temperature pri svjetlosno aktiviranoj polimerizaciji. Budući da su svi eksperimentalni kompoziti sadržavali slične volumne udjele smole (48 – 52 %) i zato usporedive količine C = C veza dostupnih za konverziju u jednostruke veze, uočeni učinak može se objasniti smanjenjem stupnja konverzije s povećanjem težinskih udjela BG-a. Navedeni učinak opisan je u preliminarnom istraživanju (18) i smatra se da potječe od inhibicije polimerizacije posredovane slobodnim radikalima djelovanjem oksida na površini čestica BG-a (30).

Iako je poznato da prekomjerni toplinski podražaji mogu štetno utjecati na zubnu pulpu, nisu definirane kritične vrijednosti temperaturnog porasta koje bi upućivale na moguća ireverzibilna oštećenja. U istraživanjima svojstva zubne pulpe da preživi porast temperature, određeni su porasti od 5,5 i 11 °C (31, 32) kao moguće granične vrijednosti za razlikovanje nepovratnog od povratnog oštećenja pulpe. Valjanost obiju spomenutih vrijednosti upitna je (33) zbog metodoloških manjkavosti prvog istraživanja (31) i činjenice da intaktni zubi ispitivani u drugom istraživanju (32) nisu reprezentativan uzorak za situaciju koja se pojavljuje u kliničkom radu. Zato do danas ne postoji definirana referentna temperatura koja bi upozoravala na nepovratna pulpna oštećenja. Čak i kad bi referentne vrijednosti bile definirane, bilo bi teško prevesti vrijednosti temperature izmjerene u uvjetima *in vitro* u klinički relevantne poraste temperature unutar pulpne komorice, s obzirom na velik broj čimbenika koje treba uzeti u obzir. Primjerice, svi su navedeni čimbenici važni: debljina preostalog dentina na pulpnom zidu, količina cakline i dentina koji okružuju kavitet, sadržaj vode u dentinu koji određuje njegovo svojstvo pufiranja topline, toplinska vodljivost dentina, volumen pulpnog tkiva i protok krvi kroz pulpu. Kako je nemoguće odvojeno prosuditi učinak pojedinih čimbenika, porast temperature unutar pulpne komorice tijekom polimerizacije kompozita u kliničkim uvjetima nije moguće odrediti. Zato je jedini način za procjenu potencijalnog oštećenja zubne pulpe, zagrijavanje tijekom svjetlosno aktivirane polimerizacije eksperimentalnih kompozita, bila usporedba s vrijednostima temperaturnog porasta komercijalnih materijala (23) koji se godinama uspješno upotrebljavaju u kliničkoj praksi i za koje je potvrđeno da su sigurni za zubnu pulpu ako se njima ispravno postupa (34). Stoga su porasti temperature izmjereni za komercijalne materijale TEC,

The approach of two consecutive illuminations (Figure 1) was adopted according to a previous study which demonstrated its usefulness for separating thermal contributions of curing unit and reaction exotherm (23). The statistical analysis showed that temperature differences among composites were mostly attributable to the reaction exotherm, while the heating effect of the curing unit was comparable in all composites due to their similar thermal capacity (Figure 2). Thus the tendency of the temperature values reached during light-curing (T_1) to decline as the BG fraction increased practically reflects a similar pattern observed for T_{exotherm} . The effect of various BG fractions produced more statistically significant differences for T_{exotherm} compared to T_1 due to lower data variability of the former. In any case, it is apparent that the BG fraction had an effect on the temperature rise during polymerization. Since all of the experimental composites had similar resin volume fractions (48-52%) and thus comparable amounts of C=C bonds available for conversion into single bonds, the observed effect could be explained by the tendency of the degree of conversion to decrease with the increasing BG filler fraction. This effect was identified in a preliminary study (18) and is hypothesized to originate from the inhibition of free radical polymerization by the oxides on the surface of BG particles (30).

Although excessive thermal stimuli are known to be harmful to dental pulp, no concrete critical threshold temperature value has been defined which would separate reversible from irreversible pulpal damage. Some studies on the pulpal capability to survive a thermal insult suggested the intrapulpal temperature increase of 5.5 and 11 °C (31, 32) as possible threshold values for distinguishing the irreversible from reversible pulpal damage. The validity of both of these values has been questioned in the dental literature (33) since the former study is considered methodologically flawed and in the latter the measurements were made on intact teeth and may not represent conditions encountered clinically. Therefore, as to date, the reference temperature value which would indicate irreversible pulpal damage remains unknown. Even if such a threshold value was defined, it would be very difficult to translate the temperature changes measured in composite specimens *in vitro* to the clinically relevant intrapulpal temperature since the influence of many factors needs to be taken into account. For example, all of the following factors play a role: remaining denting thickness at the pulpal wall, amount of the dentin and enamel surrounding the cavity, dentine water content which governs its thermal buffering capability, dentine thermal conductivity, the volume of pulpal tissue and pulpal blood flow. Since it is impossible to measure all these factors individually, the intrapulpal temperature rise occurring during the composite polymerization in a clinical setting cannot be identified. Thus, the only way to assess the potential of experimental composites to thermally damage dental pulp is through the comparison of their temperature rise to that produced by long-standing and clinically successful commercial composites (23). Since the established commercial composites are considered safe for dental pulp if handled properly (34), the temperature increase that occurred during their light-curing *in vitro* was used as a refer-

TEF i Gradia poslužili kao referentne vrijednosti za eksperimentalne kompozite.

Nano- i mikrohibridni komercijalni kompozit pokazali su slične vrijednosti temperaturnog porasta tijekom osvjtljivanja koje su bile statistički značajno niže negoli u tekućem kompozitu (slika 2.). Navedena razlika može se pripisati većem udjelu smolaste komponente u tekućem materijalu (tablica 2.), što je rezultiralo većom količinom dvostrukih C = C veza raspoloživih za egzotermnu reakciju polimerizacije. Takvo objašnjenje podupire i nalaz vrijednosti T_{exotherm} koje su u TEF materijalima bile dvostruko više negoli u materijalima TEC-a i Gradije. Eksperimentalni kompoziti BG-20 i BG-40 pokazali su vrijednosti temperaturnog porasta tijekom osvjtljivanja usporedive s referentnim vrijednostima izmjerenih za tekući komercijalni kompozit, a eksperimentalni kompoziti s nižim udjelima BG-a dosegili su vrijednosti temperature koje su bile do 1,8 °C više od referentnih. Iako je navedena razlika bila statistički značajna, upitano je kliničko značenje dobivenih rezultata. Potrebno je napomenuti da su značajno veće vrijednosti temperaturnog porasta u rasponu od 6,6 do 14,1 °C (35) i od 5,8 do 14,0 °C (36) bile izmjerene u istraživanjima komercijalnih kompozita, uz primjenu sličnog eksperimentalnog postava kao i u ovom radu. Nadalje, znatno veće vrijednosti temperaturnog porasta (do 43 °C) izmjerene su za komercijalne kompozite uporabom skenirajućeg infracrvenog sustava (37). Zato se u kontekstu podataka iz literature može zaključiti da je porast temperature tijekom svjetlosne aktivacije polimerizacije eksperimentalnih BG-kompozita bio unutar raspona vrijednosti izmjerenih za komercijalne kompozite.

Iz temperaturnih krivulja snimljenih tijekom polimerizacije u stvarnom vremenu može se dobiti informacija o dinamici porasta temperature unutar uzorka. U eksperimentalnim kompozitnim materijalima uočeni su različiti oblici temperaturnih krivulja čije su vršne vrijednosti postajale sve šire i pomicala se prema kasnijim vremenima s porastom udjela BG-a (slika 3. a). Takav rezultat upućivao je na sporiji i postupan porast temperature u kompozitima s većim udjelima BG punila. Kako bi se kvantificirale navedene razlike, određeno je vrijeme vršnih vrijednosti temperaturnog porasta, a rezultati su prikazani na slici 4. Vidljivo je da se vrijeme vršnih vrijednosti temperature značajno produljuje u kompozitima s višim udjelima BG punila. Oblik temperaturne krivulje za tekući komercijalni kompozit (TEF) bio je sličan kao za eksperimentalne kompozite, a za nano- i mikrohibridne komercijalne kompozite (TEC i Gradia) nije zabilježena vršna vrijednost temperaturnog porasta, nego samo kontinuirani porast tijekom cijelog razdoblja osvjtljivanja (slika 3. b). Navedena razlika može se objasniti činjenicom da su nano- i mikrohibridni kompoziti (TEC i Gradia) imali najniže vrijednosti T_{exotherm} od svih ispitanih materijala, što je rezultiralo prikrivanjem toplinskog učinka egzotermne reakcije mnogo izraženijim zagrijavanjem polimerizacijskim uređajem. Zato u temperaturnim krivuljama navedenih materijala nije bila vidljiva izdvojena vršna vrijednost.

Na temelju opaženoga sistematskog utjecaja udjela BG punila na temperaturni porast zbog egzotermne reakcije i vrijeme vršne vrijednosti temperaturnog porasta (slike 2. i 4.), ovisnost je analizirana Pearsonovom analizom korelacije (sli-

ence value for comparison with experimental materials.

Nano- and micro-hybrid commercial composites demonstrated similar values of temperature rise during light-curing which was significantly lower than that in the flowable composite (Figure 2). This difference can be attributed to a higher fraction of the resinous component in the flowable composite (Table 2), resulting in more C=C bonds available for the exothermic polymerization reaction. This explanation is supported by T_{exotherm} values being twice higher in TEF compared to TEC and Gradia. Experimental composites BG-20 and BG-40 showed values of temperature rise during light-curing similar to those of the flowable reference composite, while the composites with lower BG fraction reached temperature values up to 1.8 °C higher. Although the difference was statistically significant, its clinical importance is questionable. It should be noted that temperature ranges of 6.6-14.1 °C (35) and 5.8-14.0 °C (36) were reported in studies with similar experimental setups as in the present study, while much higher temperature rise (up to 43 °C) was measured in a study using infrared scanning system (37). Thus, within the context of the literature data, the temperature rise during light-curing produced by the experimental BG-containing composites was within the range of commercial composites.

The real-time plots of temperature rise during light-curing provide information on the dynamics of temperature buildup. In experimental composites, different shapes of temperature curves were identified (Figure 3a); the temperature peaks showed a tendency to widen and shift to later times as the BG fraction increased, suggesting a slower and more gradual temperature buildup in composites with higher BG fractions. To quantify this behavior, the time at which the temperature peaks occurred was determined and presented in Figure 4. The time of temperature peaks prolonged significantly as a function of higher BG fractions. The flowable commercial composite (TEF) showed a temperature peak similar to that observed in experimental composites, unlike the nano- and micro-hybrid commercial composites (TEC and Gradia) which showed no distinct temperature peak during the light-curing but rather a gradual temperature increase throughout the curing period (Figure 3b). This difference is attributable to TEC and Gradia presenting with the lowest T_{exotherm} of all the materials which resulted in the polymerization exotherm being masked by the more pronounced heating effect of the curing unit. Hence, a separate temperature peak was not distinguishable in these materials.

Since temperature rise due to the polymerization exotherm (T_{exotherm}) and time needed to reach the temperature peak appeared to be systematically influenced by the BG fraction (Figure 2 and 4), these parameters were analyzed using Pearson correlation analysis (Figure 5). The finding that both the T_{exotherm} and the time of the temperature peak were strongly correlated to the BG fraction suggests a possible impact of BG fillers on composite polymerization. The negative correlation between the BG fraction and T_{exotherm} could be related to the aforementioned effect of BG to affect the degree of conversion. The correlation of the time of temperature peak and BG fraction implies that composites with higher BG fractions not only released less heat but were also slower in

ka 5.). Nalaz jake i statistički značajne korelacije udjela BG punila s oba parametra upućuje na mogući učinak BG-a na kinetiku polimerizacije smolaste matrice. Negativna korelacija između udjela BG punila i T_{exotherm} može se povezati s već opisanim učinkom BG punila na stupanj konverzije. Pozitivna korelacija vremena vršne vrijednosti temperature i udjela BG punila upućuje na to da kompoziti s većim udjelima BG punila ne razvijaju samo manju količinu topline nego i sprije postizu maksimalne vrijednosti temperaturnog porasta, što omogućuje više vremena za disipaciju topline. Na temelju tih rezultata odbačena je prva i druga nulta hipoteza. Treća nulta hipoteza djelomično je odbačena, s obzirom na to da je porast temperature tijekom svjetlosno aktivirane polimerizacije materijala BG-20 i BG-40 bio sličan vrijednostima izmjerenima za komercijalne materijale TEF-a.

Zaključci

Eksperimentalni kompoziti s visokim težinskim udjelima BG punila (20 i 40 %) pokazali su porast temperature sličan komercijalnim kompozitima. Više vrijednosti porasta temperature tijekom osvjetljivanja izmjerene su u eksperimentalnim materijalima s nižim težinskim udjelima BG punila (0 – 10 %), ali navedene vrijednosti bile su unutar raspona temperaturnog porasta izmjerenog u komercijalnim kompozitima u ranijim istraživanjima. Zato se može pretpostaviti da će zubna pulpa podnositi porast temperature pri svjetlosnoj polimerizaciji BG-kompozita. Povećavanje udjela BG-a u eksperimentalnim kompozitima rezultiralo je smanjenjem temperaturnog porasta tijekom svjetlosno aktivirane polimerizacije i povećanjem vremena pri kojem temperaturni porast postigne maksimalnu vrijednost, upućujući na sustavni učinak udjela BG punila na kinetiku polimerizacije.

Zahvale

Kompozitne materijale Tetric EvoCeram i Tetric EvoFlow donirala je tvrtka Ivoclar Vivadent.

Sukob interesa

Autori nisu naveli sukob interesa.

reaching the maximum temperature values, providing more time for heat dissipation by dental hard tissues and pulpal tissue. These findings led to the rejection of the first and the second null hypotheses. However, the third null hypothesis was partially rejected since the temperature rise during curing of BG-20 and BG-40 was statistically similar to that of TEF.

Conclusions

Experimental composites with high BG fractions (20 and 40 wt. %) showed the temperature rise during polymerization similar to that of the commercial reference composite. A slightly higher temperature rise was measured in experimental composites with lower BG fractions (0-10 wt %); however, the obtained temperature values were within the range of commercial composites reported in previous studies. Thus the amount of heat released by experimental composites can be considered tolerable by dental pulp. Increasing the BG fraction in experimental composites decreased the temperature rise during curing and increased the time of temperature peak in a linear manner, suggesting a systematic effect of BG fraction on polymerization kinetics.

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Conflict of interest

None declared

Abstract

Objective: To investigate the real-time temperature rise during light-curing of experimental composite materials containing bioactive glass 45S5 (BG) and compare it to the temperature rise in three commercial composites. **Materials and methods:** Five light-curable composite materials containing 0-40 wt% of BG and a total filler load of 70 wt% were prepared. Cylindrical composite specimens 6 mm in diameter and 2 mm thick were cured using Bluephase G2 (Ivoclar Vivadent) at 1200 mW/cm² for 30 s. The rise in temperature during light-curing was measured at the bottom of the specimens using a T-type thermocouple at the data collection rate of 20 s⁻¹. An additional illumination for 30 s was performed after the specimen temperature returned to the baseline in order to record the temperature rise due to the heating from the curing unit. Statistical analysis was performed using the one-way ANOVA and Pearson correlation analysis with $\alpha=0.05$. **Results:** Temperature rise during light-curing of experimental composites amounted to 12.2-14.0 °C and was comparable to that of the flowable commercial composite (12.5 °C) but higher than that of nano- and micro-hybrid commercial composites (9.6-10.3 °C). The temperature rise during the second illumination was similar for all composites (7.8-9.1 °C). In experimental composites, the temperature rise which was attributable to the polymerization exotherm amounted to 3.1-5.8 °C and was negatively correlated to the BG fraction ($R^2=0.94$). Times at which temperature reached maximum values were in the range of 6.5-19.8 s and were positively correlated to the BG fraction ($R^2=0.98$). **Conclusions:** Temperature rise during light-curing of experimental composites was comparable to that of commercial composites, suggesting that the amount of heat released is tolerable by dental pulp.

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