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Utjecaj različitih vrsta punila na stupanj polimerizacije ACP-kompozitnih materijala

Influence of Different Types of Fillers on the Degree of Conversion of ACP Composite Resins

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Sažetak

Kompozitnim materijalima koji sadržavaju amorfni kalcijev fosfat (ACP) kao aktivni remineralizirajući sastojak dodana su inertna punila kako bi se smanjilo njihovo polimerizacijsko skupljanje i poboljšala mehanička svojstva. **Svrha:** Svrha istraživanja bila je ispitati utjecaj dodavanja različitih vrsta siliniziranih anorganskih punila na stupanj polimerizacije (SP) kompozita temeljenih na ACP-u. **Materijal i postupci:** Testirano je sedam ACP-kompozita: ACP-kontrola (40 % ACP, 60 % smola) i šest koji su sadržavali 40 posto ACP-a, 5 posto ili 10 posto neaktivnih punila i 55 posto ili 50 posto smole. U kompozitne materijale uključena su silika-punila (12nm; 4 – 6% silanizacija) te barijeva (0,77μm; 6% silanizacija) ili stroncijeva staklena punila (0,99μm; 3,2% silanizacija). Nanohibridni kompozit CeramX (Dentsply DeTrey, Njemačka) također je služio kao kontrolni materijal. Kompozitni uzorci (10/ispitnoj skupini) polimerizirani su 40 sekundi uređajem Bluephase C8 (Ivoclar Vivadent, Liechtenstein). Stupanj polimerizaciuje određen je Fourier transform infracrvenom spektroskopijom (System 2000 FTIR spectrometer; Perkin Elmer, Velika Britanija) 20 minuta i 72 sata nakon polimerizacije. **Rezultati:** Dodavanje 10 posto silika-punila (74,14% i 75,90%) i 5 posto stroncijevih staklenih punila (76,23% i 76,29%) nije štetno utjecalo na stupanj polimerizacije ACP-kompozitnih smola. Kod obaju kompozitnih materijala s dodanim barijevim punilima smanjio se SP u odnosu na ACP-kontrolu. Kako se i očekivalo, ACP-kontrola s najmanjim volumenom punila zadržala je najviši SP (75,38% i 76,05%), a CeramX je imao statistički najniži (56,87% i 57,97%). **Zaključak:** Iako je primjesa određenih punila pridonijela smanjenju stupnja polimerizacije ACP-kompozitnih smola, uzimajući u obzir da je ipak uvelike nadmašen stupanj polimerizacije komercijalno dostupnog kontrolnog materijala, može se zaključiti da neće izazvati neželjene učinke povezane s niskim SP-om.

Uvod

Skupina amorfnih kalcijevih fosfata (ACP-a) jedinstvena je u razredu kalcijevih ortofosfata koji su, kroz složeni proces biomineralizacije, odgovorni za stvaranje unutarnjeg skeleta i zuba ljudi. Općenito se smatra da je ACP izravni prekursor u stvaranju hidroksilapatita (1). Naime, kad se izloži djelovanju vode, ACP otpušta dostatne količine kalcijevih i fosfatnih iona kako bi se stvorio hidroksilapatit (2).

U prošlom desetljeću razvijeni su eksperimentalni kompozitni materijali koji su sadržavali ACP kao punilo kako bi poslužili kao remineralizacijsko sredstvo sposobno obnoviti oštećenu kristalnu strukturu hidroksilapatita. Demonstrirana je remineralizacija umjetno demineraliziranih ljudskih i govedih zuba (3,4), a remineralizacijski potencijal procije-

Introduction

The group of amorphous calcium phosphates (ACP) is unique in the class of calcium orthophosphates, responsible for formation of internal skeleton and human teeth through the complex process of biomineralization. It is generally considered that the ACP is a direct precursor in the formation of biological apatite (1). When exposed to water, ACP releases calcium and phosphate ions in sufficient amounts to form hydroxyapatite (2).

In the past decade, experimental composite resins containing ACP as a filler phase have been developed to serve as a remineralizing agent able to rebuild the defected hydroxyapatite crystal structure. The remineralization of artificially demineralized human or bovine teeth has been demonstrat-

njen je analizom koncentracija kalcijevih i fosfatnih iona otpuštenih iz ACP-kompozita (5,6). Ipak, ACP nije osnažujuće punilo poput silaniziranih staklenih ili silika-punila kakva se rabe u većini komercijalno dostupnih stomatoloških kompozitnih materijala. Njihova mehanička svojstva su stoga nedostatna za osiguranje potpore visokog okluzijskog tlaka kad bi se ACP-kompoziti rabili za direktne kompozitne restoracije. Uz to, visoko polimerizacijsko skupljanje te vrste materijala pripisuje se niskom udjelu punila (40%) u odnosu na 70 do 80 posto kod drugih kompozitnih materijala (7,8). Kako bi se poboljšala otpornost na mastikatorne sile te smanjile negativne posljedice polimerizacijskog skupljanja i polimerizacijski stres, formulaciji ACP-materijala dodana su inertna punila.

S druge strane, ACP-kompoziti obično pokazuju visok stupanj polimerizacije (SP-a), jednak ili veći od ostalih kompozitnih materijala dostupnih na tržištu (2, 9, 10). Pod općenito prihvaćenim uvjetima polimerizacije, SP komercijalnih kompozitnih materijala obično iznosi od 55 do 75 posto (11–4). Kako se ACP-kompoziti smatraju bioaktivnim materijalima, iznimno je važno očuvati njihovu visoku biokompatibilnost smanjujući količinu potencijalno štetnih zaostalih nereagiranih monomera (15, 16). Na stupanj polimerizacije je utječe niz čimbenika koji uključuju sastav smole i punila, koncentraciju visokoviskoznih monomera i inicijatora polimerizacije, nijansu boje kompozita, opaknost punila, intenzitet svjetlosti polimerizacijskih uređaja, vrijeme polimerizacije i mnogi drugi (17, 18). Osim dobro poznate inverzne korelacije SP-a i polimerizacijskog skupljanja kompozita (17, 19, 20), SP se također povezuje s različitim fizičkim i mehaničkim svojstvima materijala: tvrdoćom, savojnom, tlačnom i vlačnom čvrstoćom, itd (17, 20).

Etoksilirani bisfenol A dimetakrilat (EBPADMA), relativno hidrofobni analog bisfenol A glicidil dimetakrilata (bis-GMA), upotrijebljen je kao temeljni monomer za sve ACP-materijale testirane u ovom istraživanju. Stomatološki polimeri temeljeni na EBPADMA-u obično pokazuju viši SP i niže polimerizacijsko skupljanje nego oni temeljeni na bis-GMA-u zbog veće fleksibilnosti i hidrofobnosti te zbog niže viskoznosti i veće koncentracije vinilnih skupina (2).

Količina punila, njihova veličina i količina silana na punilu izravno su povezani sa smanjenjem SP-a kompozitnih materijala (22–24). Utjecaj količine punila pripisuje se apsorpciji i raspršenju svjetlosti, posebice ako je veličina čestica punila bliska izlaznoj valnoj duljini fotopolimerizacijskog uređaja (24, 25). U novijim studijama tvrdi se da količina punila nije vezana za SP, nego njihova veličina i površina (17, 20). To je osobito važno za kompozite koji se sastoje od nano-punila s velikom površinom čestica kod kojih je smanjena pokretljivost monomera u uvjetima visoke viskoznosti, što vodi nižem SP-u (26). Kako su pokazali Halvorson i suradnici (22), SP 50:50 mješavine bis-GMA i trietilen glikol dimetakrilata (TEGDMA) najviši je s dodatkom nesilaniziranih punila, a najniži kad se dodaju punila s najvećom količinom silana. Pojava je objašnjena površinskim interakcijama punila s visoko kondenziranom silaniziranom interfazom i smolaste matrice. Progresivno smanjenje SP-a u kompozitnim pastama s povećavajućim količinama silana objašnjeno

ed (3, 4) and the remineralization potential has been estimated by analyzing the calcium and phosphate ion release concentrations (5, 6). However, ACP is not a reinforcing filler such as silanized glass and silica fillers used in most of commercially available dental composite resins. The mechanical properties will therefore be insufficient to provide support for high occlusal load if the ACP composites are used as direct composite restorations. Additionally, high polymerization shrinkage of this group of materials is assigned to the low filler content (40%), compared to the 70-80% in other composite materials (7, 8). Inert fillers have been added to the formulation of ACP materials in order to improve the resistance to masticatory forces, as well as to minimize the negative effects of the polymerization shrinkage and polymerization stress.

On the other hand, ACP composite resins usually exhibit high degree of conversion (DC) equal or higher than other composite resins available at the market (2, 9,10). Under generally accepted curing protocols, DC of commercial composites ranges from 55-75% (11-14). Since ACP composites are considered to be bioactive materials, it is extremely important to maintain their good biocompatibility by minimizing the potentially harmful residual unreacted monomers (15, 16). DC is influenced by a variety of factors, including matrix and filler composition, diluent and initiator concentration, composite shade, filler opacity, light intensity of photopolymerization unit, curing time and many others (17, 18). Apart from the well-known inverse correlation of DC and the composite polymerization shrinkage (17, 19, 20), DC is also associated to various physical and mechanical properties of the material: hardness, flexural strength, compressive strength, tensile strength, etc. (17, 21).

Ethoxylated bisphenol A dimethacrylate (EBPADMA), a relatively hydrophobic analog of bisphenol A glycidyl methacrylate (bis-GMA), was used as base monomer for all ACP materials tested in this study. Dental polymers based on EBPADMA usually show higher DC and lower polymerization shrinkage than bis-GMA due to their greater flexibility and hydrophobicity, as well as lower viscosity and vinyl group concentration (2).

The amounts of filler, filler size, as well as the amount of silane on the filler are directly related to the reduction in the DC of composite pastes (22-24). The influence of filler loading is attributed to light absorption and light scattering, especially if the sizes of filler particles are close to the output wavelength of the photopolymerization unit (24, 25). Several recent studies claim that filler content is not related to the DC, but to the filler size and surface area (17, 20). This is especially important for composites comprising nano-fillers with large surface area, in which the monomer mobility is reduced in conditions of high viscosity, leading to lower DC (26). As shown by Halvorson and others (22), the DC of the bis-GMA and triethylene glycol dimethacrylate (TEGDMA) 50:50 mixture is the highest with admixture of unsilanized fillers, and the lowest when fillers with the highest amount of silane were added. This is explained by the filler surface interactions to the resin matrix of highly condensed silane interphase. Progressive decrease of DC in pastes with increasing

je smanjenom pokretljivošću silan-metakrilata i njihove re-aktivnosti (22).

Zbog specifične strukture ACP-kompozitnih materijala bilo je vrlo zanimljivo proučavati složene procese koji su posljedica interakcije silaniziranih punila, nesilaniziranog ACP-a i smolaste matrice. Svrha ovog istraživanja bila je ispitati utjecaj dodavanja različitih vrsta silaniziranih anorganskih punila na stupanj polimerizacije ACP-kompozita.

Materijali i postupci

Sinteza cirkonijskih ACP-punila

Sinteza Zr-ACP punila slijedila je postupak koji je opisao Skrtic sa suradnicima (2). Zr-ACP trenutačno je precipitirao u zatvorenom sustavu na 23°C nakon brzog miješanja jednakih volumena 800 mmol/L Ca(NO$_3$)$_2$ otopina, 536 mmol/L Na$_2$HPO$_4$ otopine koja je sadržavala molarnu frakciju od 2 posto Na$_4$P$_2$O$_7$ kao stabilizirajuće komponente za ACP i prikladnog volumena 250 mmol/L ZrOCl$_2$ otopine (molarna frakcija od 10% bazirana na kalcijskom reaktantu) (2). Reakcijski pH varirao je između 8,6 i 9,0. Suspenzija je filtrirana; čvrsta faza isprana je nakon toga ledenom amoniziranom vodom i acetonom te liofilizirana. ACP je čuvan u eksikatoru kako bi se izbjeglo izlaganje vlazi i prijevremena konverzija u apatit do korištenja u pripremi kompozita.

Priprema smole

Eksperimentalna smola pripremljena je od komercijalno dostupnih stomatoloških monomera i fotooksidanta kamforkinona (CQ) i fotoreducensa etil-4, N, N-dimetilamino benzoata (4E). Sastav je u tablici 1. Rabeći magnetnu miješalicu, monomeri i fotoaktivatori su zamiješani (bez plavog svjetla) dok se nije postigla jednakomjerna konzistencija.

ACP kompozitne paste i kontrolni materijal

Sastavi sedam ACP-kompozitnih materijala rabljenih u ovom istraživanju prikazani su u tablici 2. ACP punila (5–8 µm, nesilanizirani), različite vrste silaniziranih inertnih punila (tablica 3.) i smola zamiješani su u svjetlosno nepropusnim posudama s pomoću Speed Mixera TM DAC 150 FVC (Hauschild & Co KG, Hamm, Njemačka) na 2700 rpm tijekom 135 sekundi. Tako dobivene kompozitne paste zatim su prešane tri puta prolaskom kroz uređaj EXAKT 50 s trima valjcima (EXAKT, Norderstedt, Njemačka) kako bi se osigurala

silane amount is explained by the reduced mobility of silane methacrylate and hence its reactivity (22).

Due to the specific structure of the ACP composite resins, it was very interesting to study the complex occurrences as a result of the interaction of silanized fillers, unsilanized ACP and resin matrix. The aim of the study was to examine the influence of addition of different types of silanized inorganic fillers on the DC of the ACP composites.

Materials and Methods

Synthesis of zirconia ACP fillers

The synthesis of Zr-ACP fillers followed the procedure by Skrtic et al. (2). Zr–ACP precipitated instantaneously in a closed system at 23 °C upon rapidly mixing equal volumes of a 800 mmol/L Ca(NO$_3$)$_2$ solution, a 536 mmol/L Na$_2$HPO$_4$ solution which contained a molar fraction of 2% Na$_4$P$_2$O$_7$ as a stabilizing component for ACP, and an appropriate volume of a 250 mmol/L ZrOCl$_2$ solution (molar fraction of 10% based on the calcium reactant) (2). The reaction pH varied between 8.6 and 9.0. The suspension was filtered; the solid phase was washed subsequently with ice-cold ammoniated water and acetone and then lyophilized. ACP fillers were kept in a desiccator to avoid exposure to humidity and premature conversion to apatite until being used in preparation of composites.

Formulation of resin

The experimental resin was formulated from commercially available dental monomers and the photo-oxidant camphorquinone (CQ) and photo-reductant ethyl-4, *N, N*-dimethylamino benzoate (4E). The composition of the resin is given in Table 1. Using a magnetic mixer, the monomers and photo-activators were mixed (in the absence of blue light) until a uniform consistency was achieved.

ACP composite pastes and control material

The compositions of seven ACP composite materials used in this study are shown in Table 2. The ACP fillers (5-8 µm, unsilanized), different types of silanized inert fillers (Table 3) and resin were mixed in lightproof containers in Speed Mixer TM DAC 150 FVZ (Hauschild & Co KG, Hamm, Germany) at 2700 rpm for 135 sec, followed by pressing of the composite pastes through EXAKT 50 three roll mill (EXAKT, Norderstedt, Germany) for three times to ensure the homogeneity of pastes. The primary particle size of silica fill-

Tablica 1. Sastav smole ACP-materijala
Table 1 Resin composition of the ACP materials

Komponente smole • Resin components	Proizvođač • Manufacturer	Akronim • Acronym	tež. • wt. %	Ref. indeks • Ref. index (nD20)
Etoksilirani bisfenol A dimetakrilat • Ethoxylated bisphenol A dimethacrylate	Esstech, PA, SAD • USA	EBPADMA	62.8	1.535
Trietilen glikol dimetakrilat • Triethylene glycol dimethacrylate	Esstech, PA, SAD • USA	TEGDMA	23.2	1.459
2-hidroksietil metakrilat • 2-hydroxyethyl methacrylate	Esstech, PA, SAD • USA	HEMA	10.4	1.452
Metakriloksietil ftalat • Methacryloxyethyl phthalate	Esstech, PA, SAD • USA	MEP	2.6	1.526
Kamforkinon • Camphorquinone	Aldrich, WI, SAD • USA	CQ	0.2	/
Etil-4-N,N-dimetilaminobenzoat • Ethyl-4-N,N-dimethylaminobenzoate	Aldrich, WI, SAD • USA	4E	0.8	/

Tablica 2. Sastav ACP-materijala Table 2 Composition of the ACP materials	Materijal • Material	ACP (tež. %) • ACP (wt %)	Smola (tež. %) • Resins (wt %)	Inertna punila (tež. %) • Inert fillers (wt %)
	ACP-kontrola • ACP control	40	60	0
	5% Ba	40	55	5
	10% Ba	40	50	10
	5% Sr	40	55	5
	10% Sr	40	50	10
	5% Si	40	55	5
	10% Si	40	50	10

Tablica 3. Specifikacije inertnih punila dodanih ispitivanim ACP-materijalima
Table 3 Specifications of inert fillers added to the ACP test materials

Punila • Fillers	Sastav • Composition	Veličina • Size (d50/d99 [µm])*	Silanizacija (tež. %)* • Silanization (wt %)*	Refraktivni indeks • Refractive index (nD20)	Naziv proizvoda/Proizvođač • Product name/Manufacturer
Barij staklo • Barium glass (Ba)	Al_2O_3 10.0 % B_2O_3 10.0 % BaO 25.0 % Fluorine, F 2.00 % SiO_2 55.0 %	0.77/2.28	6	1.52	GM39923 Schott, Njemačka • Gemany
Stroncij staklo • Strontium glass (Sr)	Al_2O_3 15.0 % B_2O_3 15.0 % Fluorine, F 2.00 % SiO_2 60.0 %	0.99/2.95	3.2	1.50	G018-163 Schott, Njemačka • Gemany
Silika • Silica (Si)	$SiO_2 \geq 99.8$	12/**	4-6	**	Aerosil DT, Evonik Degussa, Njemačka • Germany

* Podaci dobiveni od proizvođača • Data provided by the manufacturer
** Nepoznati podaci • Data not provided

homogenost smjese. Primarna veličina čestica silika punila je 12 nm, no one ne postoje u izoliranoj formi i aglomerirane su u skupine približne veličine 12 µm (osobna komunikacija s proizvođačem).

Kao vanjski kontrolni materijal služio je nanohibridni kompozit CeramX (Dentsply De Trey, Konstanz, Njemačka; LOT 0910001050; datum isteka srpanj, 2011.), u nijansi Mono+M5 koja odgovara nijansi A3 u Vitinu ključu boja. Prema podacima proizvođača sastoji se od <25 posto dimeta-krilatne smole, manje od 80 posto barijeva boron alumino-silikatnog stakla i 5 posto amorfnog silicijeva dioksida.

Stupanj polimerizacije (SP)

Količina poput pola zrna riže kompozitne paste stavljena je između dviju PET-folija i pritisnuta u Carverovoj preši (Specac Ltd., Orpington, Kent, Velika Britanija) pod tlakom od 10^7 Pa. Prešani uzorci polimerizirani su u izravnom kontaktu s polimerizacijskim uređajem Bluephase C8 LED, u načinu rada visokog intenziteta tijekom 40 sekundi (1090 mW/cm², Ivoclar Vivadent, Schaan, Liechtenstein). Pripremljeno je ukupno 80 uzoraka – deset za svaki ispitivani materijal. Nepolimerizirani uzorci stisnuti su u KBr pastile (d=1 cm) koristeći se spektroskopski čistim KBr-om (Merck, Darmstadt, Njemačka) i Carverovom prešom. SP polimeriziranih uzoraka određen je s pomoću Fourier transform infracrvene spektroskopije (FTIR; System 2000 FTIR spectrometer, Perkin Elmer, Beaconsfield, Bucks, Velika Britanija), kako su detaljno opisali Z. Tarle i suradnici (27). Očitavanje i procesuiranje apsorpcijskih spektara kompozitnih uzo-

ers is 12 nm, but they do not exist as an isolated form and they are agglomerated into clusters of approximately 12 µm (personal communication from the manufacturer).

Nanohybrid composite resin CeramX (Dentsply De Trey, Konstanz, Germany; LOT 0910001050; expiration date 2011-07) in Mono+M5 shade, which corresponds to A3 in Vita shade guide, served as external control material. According to the data provided by the manufacturer, it is composed of <25% dimethacrylate resin, less than 80% of barium boron alumino silicate glass and 5% of amorphous silicon dioxide.

Degree of conversion (DC)

A half of rice grain amount of composite paste was placed between two PET sheets and pressed in Carver press (Specac Ltd., Orpington, Kent, UK) under 10^7 Pa. Pressed samples were 1 cm in diameter and 0.1 mm thick. The samples were polymerized using Bluephase C8 LED polymerization device in "high power" polymerization mode for 40 seconds (1090 mW/cm², Ivoclar Vivadent, Schaan, Liechtenstein) in direct contact. Total of 80 samples were prepared, ten for each tested material. Uncured samples were pressed into KBr pellets (d = 1 cm) using spectroscopically pure KBr (Merck, Darmstadt, Germany) with a Carver press. DC of polymerized samples was determined by Fourier transform infrared spectroscopy (FTIR; System 2000 FTIR spectrometer, Perkin Elmer, Beaconsfield, Bucks, UK), described in detail by Tarle et al. (27). Recording and processing of absorption spectra of composite specimens were carried out with Spectrum v5.3.1

raka provedeni su koristeći se programom Spectrum v5.3.1 (Perkin Elmer, Beaconsfield, Bucks, Velika Britanija). Spektri sparenih polimeriziranih i nepolimeriziranih kompozitnih uzoraka zabilježeni su u transmisijskom modu na sobnoj temperaturi te korigirani subtrakcijom pozadine te su zatim prevedeni u apsorbancijski oblik. Učinjeno je ukupno 20 očitanja po uzorku pri rezoluciji od 4 cm^{-1}. Spektri svakog uzorka zabilježeni su 20 minuta nakon polimerizacije i nakon 72 sata. Stupanj polimerizacije izračunat je iz ekvivalentnih alifatskih (1638 cm^{-1})/aromatskih (1610 cm^{-1}) molarnih omjera polimeriziranih (P) i nepolimeriziranih (N) uzoraka prema sljedećoj formuli (28):

$$SP = (1 - P/N) \times 100 \ (\%)$$

Statistička analiza

Podaci dobiveni za stupanj polimerizacije (10 uzoraka/8 skupina/2 vremenske točke) deskriptivno su izraženi kao medijani s 25 do 75 posto kvartilana i prikazani u obliku grafa. Za statističku analizu korišteni su Mann-Whitneyjev i Wilcoxon-Rank-Sum test za usporedbu ovisnih i neovisnih eksperimentalnih skupina, svaki zasebno. Razina značajnosti postavljena je na α=0,05. Za višestruke usporedbe α je prilagođen rabeći Error-Rates Method prema formuli α* (k)=1-(1-α)$^{1/k}$, gdje k znači broj sparenih testova koji se uzimaju u obzir. Sve analize obavljene su u programu SPSS 19,0 (SPSS Inc., Chicago, SAD).

Rezultati

Rezultati stupnja polimerizacije materijala ispitivanih u ovom istraživanju 20 minuta i 72 sata nakon svjetlosne polimerizacije spojeni su u slici 1.
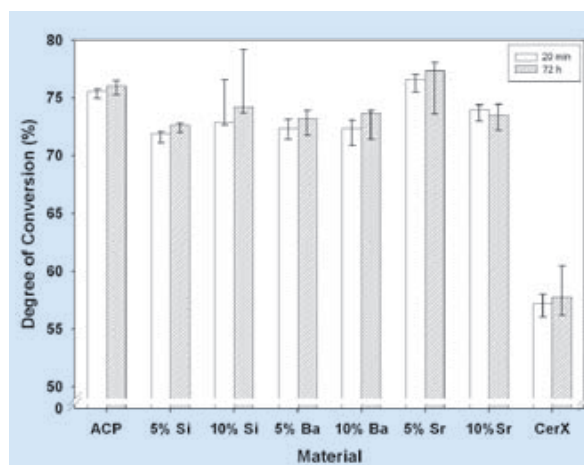
software (Perkin Elmer, Beaconsfield, Bucks, UK). Spectra of paired un-polymerized and polymerized composite specimens were recorded in a transmission mode at room temperature, corrected by subtracting the background and then converted into the absorbance mode. A total of 20 scans per sample were measured at a resolution of 4 cm^{-1}. The spectra of each sample were taken two times, 20 minutes after the polymerization of samples and after 72h. The peak ratios were calculated according to Rueggeberg's baseline method (28). Precaution was taken to eliminate the influence of moisture from the air to the samples. DC (%) was calculated from the equivalent aliphatic (1638 cm^{-1})/aromatic (1610 cm^{-1}) molar ratios of cured (C) and uncured (U) samples according to the following expression (28):

$$DC = (1 - C/U) \times 100 \ (\%)$$

Statistical analysis

The data obtained for the DC (10 samples/ 8 groups/ 2 time points) were descriptively expressed as medians with 25-75% quartiles and depicted as a graph. For the statistical analysis, Mann-Whitney test and Wilcoxon-Rank-Sum test were applied for the comparison of independent and dependent experimental groups, respectively. The level of significance was set to α=0.05. For multiple comparisons α was adjusted to α* (k)=1-(1-α)$^{1/k}$ applying the Error-Rates Method, where k stands for the number of pairwise tests to be considered. All analyses were performed using SPSS 19.0 software (SPSS Inc., Chicago, USA).

Results

The results of the DC of materials tested in this study, at 20 min (baseline) and 72 hours after photopolymerization are summarized in Figure 1.

Slika 1. Vrijednosti SP-a ispitivanih materijala 20 minuta i 72 sata nakon fotopolimerizacije
Figure 1 DC values of tested materials 20 minutes and 72 hours after photopolymerization

ACP-kontrolni materijal (75,38% i 76,05%) i 5% Sr (76,23% i 76,29%) bili su statistički najviše polimerizirani. Istaknimo da je 10 % Si (74,14% i 75,90 %) pokazalo najveći porast SP-a poslije osvjetljavanja (nakon 20 minuta i nakon 72 sata), što ga je uvrstilo u skupinu najviše polimeriziranih materijala. Za razliku od 10% Si, 5% Si bio je najmanje polimerizirani ACP-materijal. Stupanj polimeri-

The ACP control (75.38% and 76.05%), and 5% Sr (76.23% and 76.29%) were statistically the most polymerized materials. 10% Si (74.14% and 75.90%) showed the highest post-cure DC increase (20 minutes vs. 72 h), which has placed it in the group of most polymerized materials. Unlike 10% Si, 5% Si was the least polymerized ACP material. The DC of 5% Sr was higher than 10% Sr in all time points,

zacije 5% Sr bio je viši od 10% Sr u svim vremenskim toč-kama, bez značajnog porasta SP-a nakon fotopolimerizacije. Slične vrijednosti SP-a pokazalo je 5% i 10% Ba u obje mjerene vremenske točke, što je bilo statistički mnogo niže od ACP-kontrolnog materijala.

CerX (56,87% i 57,97%) bio je materijal sa značajno najnižim SP-om od svih ispitivanih materijala.

Rasprava

Ovo istraživanje ispitivalo je utjecaj triju vrsta punila različitih veličina, refraktivnih indeksa i postotka silanizacije na stupanj polimerizacije ACP-kompozitnih materijala temeljenih na EBPADMA-u. Inertna punila dodana su u kompozitne paste u 5-postotnom ili 10-postotnom iznosu. Primijećena su tri obrasca ponašanja za svaku vrstu punila: (i) formulacije s višim iznosom silika čestica pokazale su viši SP; (ii) manji iznos stroncijevih staklenih punila pridonio je višem SP-u negoli 10-postotni dodatak; (iii) kompoziti s barijevim staklenim punilima nisu pokazali razlike u pastama s dodanih 5% ili 10% barijevih punila.

Najzanimljiviji rezultat ispitivanja jest visok porast SP-a 10% Si nakon završene svjetlosne polimerizacije (74,14% – 20 minuta nakon fotopolimerizacije i 75,90 % – nakon 72 sata), zahvaljujući kojem je taj materijal "skočio" u skupinu najviše polimeriziranih materijala. Specifičnost tih nanopunila je u maloj veličini primarnih čestica i njihovoj velikoj površini kombiniranoj s visokim postotkom silanizacije. Njihova tiksotropna svojstva otežavaju dodavanje većih količina bez aglomeracije čestica (29). To je istaknuto činjenicom da ACP-čestice imaju istu tendenciju, iako su poduzete sve mjere kako bi se osigurala homogena distribucija punila korištenjem uređaja za miješanje i uređaja s valjcima. Obrnuto od 10% Si, 5% Si bilo je u skupini s najnižim SP-om. Rezultat je neočekivan jer podaci drugih istraživanja visok udjel punila povezuju s niskim SP-om. U slučaju 10% Si taj se fenomen može objasniti prevelikim dodatkom punila kako bi se postigla jednakomjerna raspodjela čestica (29). Određena količina punila vjerojatno je ostala unutar aglomerata silika-punila i na površini njihovih čestica silan nije bio dostupan za interakciju sa smolom. Dakle, aglomerati s manjom površinom i nižom silanizacijom vjerojatno su rezultirali većom pokretljivošću monomera, što se nastavilo i u poslijepolimerizacijskom razdoblju (22).

Drugo objašnjenje jest polimerizacijom inducirano razdvajanje faza. To je fenomen u kojem rastuća molekulska masa polimerne mreže uzrokuje termodinamičku nestabilnost tijekom polimerizacije koja se prevladava izdvajanjem faza komponenata koje se ne miješaju (29). Manifestira se pojavom mikrometarskih zona bogatih polimerom bez punila ili s malom količinom punila koji pokazuju viši SP-a od ostatka uzorka.

Silika-punila u 5% Si bila su, pretpostavljamo, jednakomjernije dispergirana, što je vjerojatno dovelo do fiksacije smolastih monomera nakon što je dosegnuta gel-točka. Iako je i taj materijal imao veliki porast SP-a u poslijepolimerizacijskom razdoblju, možemo pretpostaviti da je nesilanizirani ACP dopustio završno smještanje monomera.

with no significant post-cure increase in DC. 5% and 10% Ba showed similar DC values in both measured time points, which was statistically lower than in the ACP control.

CerX (56.87% and 57.97%) was the material with significantly lowest DC of all tested materials.

Discussion

This study examined the influence of three different types of fillers with different sizes, refractive indices and the silanization percentage on the degree of conversion of ACP composite resins based on EBPADMA. The inert fillers were compounded into the composite pastes in 5 or 10 wt.% amount. Three different behavior patterns were observed for each filler type: (i) formulations with higher amount of silica particles revealed higher DC; (ii) smaller amount of strontium glass fillers contributed to the higher DC than 10% addition and (iii) the composites with barium glass fillers showed no differences between the pastes with the addition 5 or 10% of Ba fillers.

The most interesting result of the study is the high post-cure DC increase of the 10% Si (74.14% 20 min after photopolymerization and 75.90% after 72 hours), owing to which this material jumped into the group of highest polymerized materials. The specificity of these nano-fillers is a small primary particle size and its large surface area, combined with relatively high silanization percentage. Their thixotropic properties make it very challenging to admix bigger quantities without the particle agglomeration (29). This is emphasized by the fact that the ACP particles have the same tendency, even though the maximum care has been taken to ensure homogeneous filler distribution by the use of both mixing and rolling machine. Contrary to 10% Si, 5% Si was in the group with the lowest DC. The result was unexpected, since the results of the other studies associate higher filler content to the lower DC. In the case of 10% Si, this phenomenon can be explained by the too high filler admixture for the uniform filler distribution (29). A certain amount of fillers was probably inside the silica agglomerates and the silane on their surface was inaccessible for the interaction with the matrix. Hence, the agglomerates with smaller surface area and lower silanization have presumably caused greater dimethacrylate monomer mobility, which also continued during the post-polymerization period (22).

Another explanation is the polymerization-induced phase separation. This is a phenomenon in which the increasing molecular mass of a polymer network in a mixed or blended system causes thermodynamic instability during polymerization which is overcome by phase separation of the immiscible components (29). This is manifested by the occurrence of micrometer sized polymer rich zones with no or small amount of fillers which show greater DC than the remainder of the sample.

The silica fillers in 5% Si were probably more evenly dispersed, which probably caused the fixation of the resin monomers after reaching the gel-point. Although there was a

Materijal s najvišim SP-om bio je 5% Sr, zajedno s kontrolnim ACP-materijalom bez dodanih punila, dok je SP bio znatno niži kod 10% Sr. Taj ishod je najočekivaniji zato što slijedi rezultate većine ostalih studija (23, 24, 30). Ukupna količina punila kod 5% Sr razmjerno je mala, stroncijeva punila su u mikro-veličini (1 µm), što znači da imaju malu površinu i najniži postotak silanizacije (3,2%) od svih punila u ovom ispitivanju.

ACP-kompozitni materijali s barijevim mikropunilima relativno visoke silanizacije (6%) ostvarili su gotovo jednak SP, bez obzira na njihovu količinu u mješavini. Niži SP kod ACP-kompozita s dodatkom 5% i 10% Ba može biti povezan s refraktivnim indeksom barijevih punila (1,52). U nekoliko istraživanja ispitivao se utjecaj nepodudaranja refraktivnih indeksa punila i smolaste faze stomatoloških punila na dubinu njihove polimerizacije (31–33). Zaključeno je da se SP može poboljšati optimizacijom refraktivnih indeksa punila i smole. Nažalost, refraktivni indeks smole u ovom ispitivanju nije utvrđen, ali možemo pretpostaviti da je refraktivni indeks bazičnog monomera EBPADMA (1,535) bio smanjen dodatkom razrjeđujućih monomera TEGDMA i HEMA koji imaju refraktivne indekse oko 1,4, slično kao u ref. (32). Može se pretpostaviti da je raskorak između EBPADMA matriksa i barijevih punila uzrokovao smanjenje u transmisiji svjetlosti. Shortall i suradnici (32) pronašli su da kompoziti s velikom razlikom između refraktivnih indeksa punila i smole izgledaju opakni. To je također bio slučaj i za 5-postotne i 10-postotne barijeve kompozite u ovom istraživanju, koji su se činili manje transparentni od drugih ACP-materijala.

Zaključak

Dodatak 5% silaniziranih stroncijevih staklenih punila nije negativno utjecao na stupanj polimerizacije. Kompozit s dodatkom 10% siliniziranih silika nano-punila također je pokazao visok stupanj polimerizacije. Svi ispitivani ACP-materijali imali su mnogo viši stupanj polimerizacije od kontrolnog komercijalnog nanohibridnog kompozita.

Zahvale

significant post-cure increase in DC within this material, we might presume that the final settling of the monomers was allowed by the unsilanized ACP.

5% Sr was the material with the highest DC, along with the control ACP without added inert fillers, whereas the DC of 10% Sr was always significantly lower. This is the most expected outcome, as it follows the results of majority of other studies (23, 24, 30). The total filler amount in 5% Sr is relatively low and Sr fillers are micro-sized (1 µm), which means that they have smaller surface area and also have the lowest silanization percentage (3.2%) of all the fillers used in this study.

The ACP composite materials with barium microfillers of relatively high silanization (6%) performed almost equally in terms of DC regardless of their amount in the mixture. The DC of both 5 and 10% Ba were at the low end of ACP composites and this effect might be related to the refractive index of the Ba glass fillers (1.52). Several studies have investigated the influence of refractive index mismatch between fillers and resinous phase of dental composite materials on their depth of cure (31-33). It was determined that the polymerization conversion can be improved by the optimizing filler/resin refractive index. Unfortunately, we have not measured the refractive index of our resins, but we may presume that the refractive index of the base monomer EBPADMA (1.535) is probably lowered by the addition of diluent monomers TEGDMA and HEMA, both with refractive indices around 1.4, similar as in ref. (32). It could be hypothesized that the disparity between the refractive indices of EBPADMA based matrix and Ba fillers caused the reduction in light transmission. Shortall et al. (32) have found that the composites with a large mismatch between filler and resin refractive indices appeared opaque. This was also the case in our study for both 5 and 10% Ba materials, which appeared less transparent than other ACP materials.

Conclusion

The degree of conversion was not negatively influenced by the addition of 5% of silanized strontium glass fillers. A composite material with the addition of 10% silanized silica nano-filler also exhibited very high degree of conversion. All tested ACP materials showed significantly higher degree of conversion than the commercial nanohybrid composite control.

Acknowledgments

Abstract

In order to diminish the polymerization shrinkage and improve mechanical properties of the composite materials containing amorphous calcium phosphate (ACP) as an active remineralizing ingredient, inert fillers were introduced into formulation. **Purpose:** The aim of the study was to examine the influence of the addition of different types of silanized inorganic fillers on the degree of conversion (DC) of the ACP based composites. **Material and Methods:** Seven ACP composites were tested: ACP control (40% ACP, 60% resin) and six composites containing 40% ACP, 5% or 10% non-releasing fillers and 55% or 50% resin. Silica fillers (12nm; 4-6% silanization), barium (0.77μm; 6% silanization) or strontium glass fillers (0.99μm; 3.2% silanization) were included into the pastes. Nanohybrid composite CeramX (Dentsply DeTrey, Germany) also served as a control. Composite specimens (10/experimental group) were polymerized for 40 sec by Bluephase C8 curing unit (Ivoclar Vivadent, Liechtenstein). The DC was determined by Fourier- transform infrared spectroscopy (System 2000 FTIR spectrometer; Perkin Elmer, UK) 20 min and 72 h after polymerization. **Results:** The addition of 10% of silica (74.14% and 75.90%) and 5% of strontium glass fillers (76.23% and 76.29%) did not have a detrimental influence on the DC of ACP composite resins. Both composites with added barium fillers showed the reduction in DC when compared to the ACP control. As expected, the ACP control with the lowest filler volume retained the highest conversion rate (75.38% and 76.05%), and CeramX had significantly lowest DC (56.87% and 57.97%). **Conclusions:** Even though the admixture of certain fillers yielded decrease of the DC of ACP composite resins, and considering the fact that it still greatly exceeded the DC of the commercial control, it might be concluded that they will not cause adverse effects associated with low DC.

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