

Svojstva kompozitnih materijala polimeriziranih pulsni laserom

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Sažetak

Svrha rada bila je raščlaniti pojedina svojstva uzoraka kompozitnih smola polimeriziranih pulsni laserom u usporedbi sa standardnom žaruljom. Tri hibridna i tri mikropunjena kompozitna materijala polimerizirani su, u eksperimentalnim uvjetima, uporabom excimer i dye lasera (XeCl Lambda Physik LPX 100/LPD 3002) i standardne halogene žarulje (Heliolux GTE). Uzorci su raščlanjeni spektroskopski (FTIR) za određivanje stupanja konverzije, scanning elektronskim mikroskopom za raščlambu strukture materijala, a ponašanje volumetrijskoga skupljanja testirano je s pomoću piknometra. Statistička raščlamba podataka (ANOVA, $p < 0,05$) pokazala je znatno veće vrijednosti stupnja konverzije dobivene pri polimerizaciji pulsni laserom za sve ispitivane materijale i boje, a rezultati polimerizacijskoga skupljanja znatno su niži u usporedbi s rezultatima dobivenim standardnom žaruljom. Ti su rezultati klinički vrlo važni u okolnostima kada je teško postići blizak doticaj uređaja za polimerizaciju i površine kompozitnog ispuna. Monokromatski pulsni laser, pri valnoj dužini od 468 nm, omogućuje snažan prodor svjetla u uzorak, a priroda pulsa osigurava homogeno, visokokvalitetno stvrdnjavanje sa smanjenim skupljanjem kompozitne smole. Osjetljivost zuba nakon aplikacije izravnoga kompozitnog ispuna većinom je povezana s polimerizacijskim skupljanjem. Adhezijske i kohezijske frakture događaju se u dentinu, hibridnom sloju i u samome materijalu. Veličina volumetrijskih promjena povezana je sa stupnjem konverzije, vrstom kompozitnoga materijala i prirodom svjetla za polimerizaciju.

Ključne riječi: kompozitne smole, laser, konverzija monomera, polimerizacijsko skupljanje

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Uvod

Postojeći svjetlosno polimerizirajući kompozitni materijali podliježu polimerizacijskom skupljanju monomera tijekom procesa stvrdnjavanja što uzrokuje adhezijske i kohezijske frakture te nastanak pukotine između materijala i zubne strukture (1). Svrha ostvarivanja optimalnih svojstava kompozitnih ispuna u suprotnosti je s postizanjem optimalnog integriteta između površine zuba i kompozita (2). Poznato je nekoliko pristupa kojima se nastoji prevladati antagonizam između stupnja konverzije i polimerizacijskog skupljanja te za redukciju stresa, kao što je uporaba dentinskih svezujućih sredstava ili stres apsorbirajućih kavitetnih premaza. Ipak, kada je postignuta čvrsta sveza, topivost dentina ili sveza između hibridnoga sloja i dentina može biti ograničavajući čimbenik njihove jakosti (3).

Razvoj stresa u adhezijskim kompozitnim ispunima ovisi o geometrijskom obliku kaviteta. Otjecanje materijala u pregelacijskoj fazi inhibirano je ako je omjer adhezijski pripremljenih stijenki spram

slobodne površine veći od određene granice (4,5). Daljnji napredak je uporaba halogene žarulje niskog intenziteta za kontrolu otjecanja materijala tijekom polimerizacije, ali i dalje ostaje znatan problem nedostatnog približavanja izvora svjetla površini kompozita (6,7). Pokušaj eliminacije polimerizacijskog skupljanja nastoji se postići sintezom monomera koji ekspaniraju tijekom polimerizacije (8-11), ali takvi monomeri još nisu inkorporirani u komercijalne dentalne materijale.

Svrha rada bila je usporediti polimerizaciju standardnom žaruljom i pulsnim laserom različitih kompozitnih materijala određivanjem:

- stupnja konverzije kompozitnih uzoraka uporabom Fourier transform infracrvene spektroskopije (FTIR);
- veličine, vrste, raspodjele i težinskog udjela punila kompozitnih uzoraka uporabom scanning elektronske mikroskopije (SEM);
- polimerizacijskoga skupljanja s pomoću piknometra.

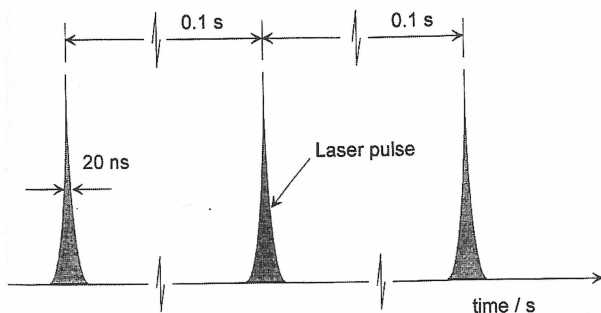
Tablica 1. Kompozitni materijali rabljeni u pokusu

Table 1. Composite materials used in the study

Kompozit Composite	Proizvođač Manufacturer	Boja Shade	Broj Batch No.	Kratica Abbreviation	Vrsta kompozita Composite type	Punilo količina % Filler vol. (%)	Vrsta punila Filler type
VALUX PLUS	3M DENTAL PRODUCTS (St. Paul MN)	svjetli light	19940725	VPA2	hybrid	71	Zirconia-silica
VALUX PLUS	3M DENTAL PRODUCTS (St. Paul MN)	tamni dark	19941109	VPCG	hybrid	71	Zirconia-silica
TETRIC	VIVADENT (Schaan, Liechtenstein)	svjetli light	660039	T20	hybrid	62	Spherosil, SiO ₂ Ba glass, YbF ₃
TETRIC	VIVADENT (Schaan, Liechtenstein)	tamni dark	614818	T24	hybrid	62	Spherosil, SiO ₂ Ba glass, YbF ₃
PERTAC HYBRID	ESPE (Seefeld, Germany)	svjetli light	0086233	PHA1	hybrid	58	Quartz, SiO ₂ , YF ₃
PERTAC HYBRID	ESPE (Seefeld, Germany)	tamni dark	0097277	PHA4	hybrid	58	Quartz, SiO ₂ , YF ₃
HELIOMOLAR	VIVADENT (Schaan, Liechtenstein)	svjetli light	660029	HM20	microfilled	46	SiO ₂ , YbF ₃
HELIOMOLAR	VIVADENT (Schaan, Liechtenstein)	tamni dark	569446	HM24	microfilled	46	SiO ₂ , YbF ₃
HELIOPROGRESS	VIVADENT (Schaan, Liechtenstein)	svjetli light	606393	HP20	microfilled	43	SiO ₂ , YbF ₃
HELIOPROGRESS	VIVADENT (Schaan, Liechtenstein)	tamni dark	604964	HP24	microfilled	43	SiO ₂ , YbF ₃
VISIO DISPERS	ESPE (Seefeld, Germany)	svjetli light	0042 W 288	VDL	microfilled	46	SiO ₂
VISIO DISPERS	ESPE (Seefeld, Germany)	tamni dark	0048 L 337	VDB	microfilled	46	SiO ₂

Materijali i metode

Hibridni i kompozitni materijali s mikropunilom, rabljeni u ovom ispitivanju, prikazani su u Tablici 1. Pulsni laser, rabljen kao izvor svjetla za fotopolimerizaciju, sastoji se od excimer lasera XeCl Lambda Physik LPX 100 i dye laser (Lambda Physik 3002, Göttingen, Germany) s Coumarin 102 bojom. Vrijeme jednoga pulsa je 20 ns, a ukupan broj pulseva 400, s razdobljem ponavljanja od 10 Hz (Slika 1), energijom od 10 mJ po pulsu i valnom dužinom od 468 nm. Kontrolno mjerenje napravljeno je uporabom Heliolux GTE (Ivoclar/Vivadent, Schaan, Liechtenstein) uređajem za polimerizaciju izlaznog intenziteta svjetla od 500 mW/cm², mjerenog Curing Radiometrom Model 100 (Demetron Research Corporation, Danbury, CT, USA). Uzorci kompozitnih materijala pripremljeni su na isti način za polimerizaciju halogenom žaruljom i pulsnim laserom (12). Nakana je bila simulirati dubinu uzorka na površini, 1,0 i 2,0 mm dubine, rabeći 1,0 mm i 2,0 mm debele nadslojeve, prethodno stvrdnute u Spectramatu PM 1831 (Ivoclar/Vivadent, Schaan, Liechtenstein) po dvije minute sa svake strane. Podslojevi iste debljine napravljeni su od istih materijala kako bi se osigurala konstantna povratna refleksija. Tanak sloj nepolimeriziranoga kompozita stavljen je između dvije Mylar folije i stlačen tlakom od 100 bara na 0,1 mm debljine. Za površinsko mjerenje nepolimerizirani uzorak smješten između dvije Mylar folije osvijetljen je 40 s, dok je za mjerenje na većoj dubini stvrdnuti nadsloj stavljen iznad gornje Mylar folije a optičko vlakno na njega te osvijetljen 40 s. U slučaju stvrdnjavanja pulsnim laserom uzorci kompozitnih materijala fiksirani su u metalnom držaču, tako i nadsloj i podsloj pri simula-



Slika 1. Trajanje laserskoga pulsa
Figure 1. Duration of the laser pulse

ciji odgovarajuće dubine. Laserski se snop, prolazeći kroz divergentnu leću, dispergira na površini 1 cm² uzorka. Vrijeme ekspozicije bilo je ponovno 40 s.

Mjerenje stupnja konverzije

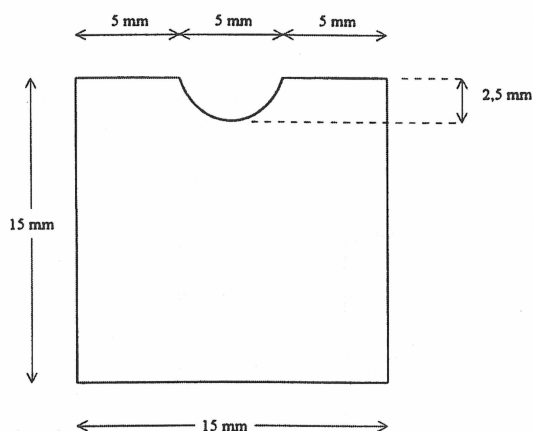
FTIR spektar polimeriziranih uzoraka snimljen je u transmisivskom modu na sobnoj temperaturi uporabom Perkin Elmer Spectrometra, Model 2000, u infracrvenom području spektra 4000-400 cm⁻¹ (Perkin Elmer, Beaconsfield, Bucks, England). Spektrometar je povezan s IR Data Manager (IRDM) programom. Nepolimerizirani uzorci pomiješani su s KBr-om (Merck, Darmstadt, Germany). Spektri su raščlanjeni nakon 20 "skenova" pri rezoluciji od 4 cm⁻¹. Omjer pikova izračunan je prema Rueggebergovoj metodi bazne linije, a stupanj konverzije izračunan je iz ekvivalenta alifatskih (1638 cm⁻¹)/aromatskih (1610 cm⁻¹) molarnih udjela polimeriziranog (P) i nepolimeriziranog (N) uzorka prema formuli (13):
% konverzije = (1 - P/N) x 100

Scanning elektronska mikroskopija

Kompozitni uzorci debljine 1 mm i promjera 25 mm presvučeni su zlatom i promatrani Digitalnim scanning mikroskopom DMS-962 (Zeiss, Jena, Germany). Raspored čestica punila raščlanjen je kompozicijskim kontrastom sa sekundarno raspršenim elektronima u pozadini. Mikrorasčlamba energetski dispergiranih X-zraka rabljena je za određivanje tipa čestica punila za hibridne kompozitne materijale.

Mjerenje polimerizacijskog skupljanja

Polimerizacijsko skupljanje u ovome je radu određeno metodom piknometra. Rabljena je vaga s točnošću od +0,00001 g (August Sauter KG, Ebingen, Germany), a mjerenja su izvedena na sobnoj temperaturi. Uzorci cilindričnog oblika približne težine 0,2 g stavljeni su u piknometar volumena 20 cm³ koji sadržava vodu (qH₂O na 25°C = 0,99707 g/cm³). Oblik i veličina uzoraka prikazani su na Slici 2. Uzorci su osvijetljeni standardnom svjetiljkom ili pulsnim laserom prije mjerenja 40 s i 120 s. Za svaki uzorak napravljena su tri uzastopna mjerenja. Gustoća uzoraka mjerena je prema formuli:



Slika 2. Kalup rabljen za pripremu uzoraka za mjerenje polimerizacijskog skupljanja

Figure 2. Mould used for the specimen preparation for polymerization shrinkage measurements

$$q = \left(\frac{C-A}{(B-A)-(E-C)} \right) \times q_{H_2O} \text{ (q/cm}^3\text{)}$$

q = gustoća materijala

A = težina piknometra

B = težina piknometra + voda

C = težina piknometra + uzorak

E = težina piknometra + uzorak + voda

Promjena gustoće između polimeriziranog i nepolimeriziranog uzorka služi za računanje volumne kontrakcije, tj. skupljanja. Postotak skupljanja S (%) računat je po formuli:

$$S = (1 - (q_N/q_p)) \times 100$$

gdje je q_N gustoća nepolimeriziranog i q_p gustoća polimeriziranog uzorka izražena u g/cm^3 .

Stupanj konverzije i rezultati polimerizacijskoga skupljanja raščlanjeni su jedno- i tro-faktorskom raščlambom varijance ($p > 0,05$). Statistički SPSS paket upotrijebljen je za grafički prikaz rezultata polimerizacijskoga skupljanja.

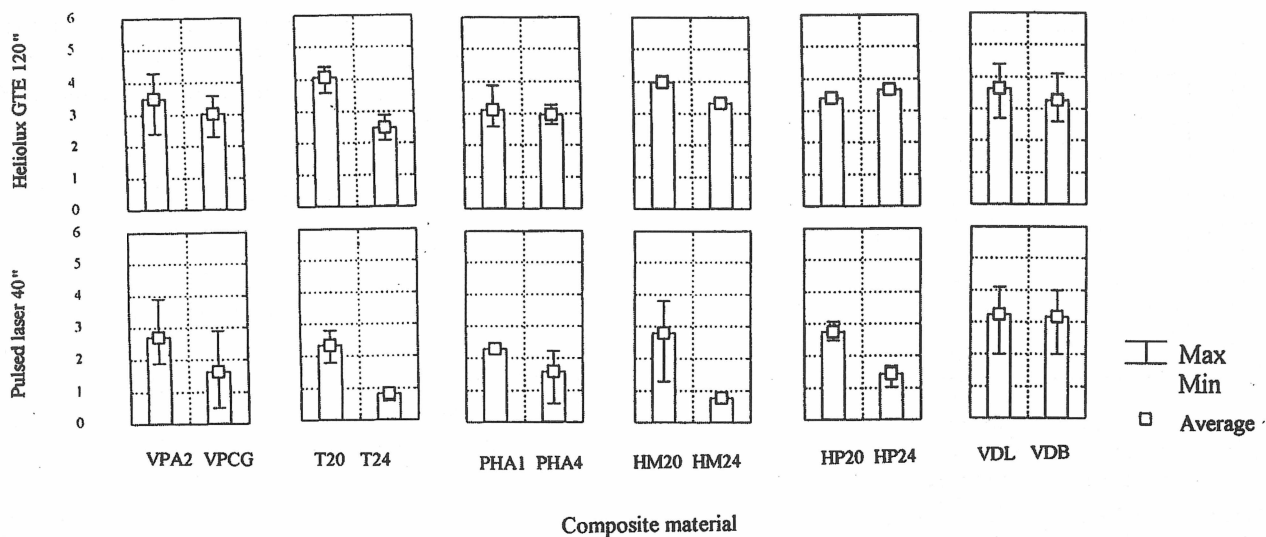
Rezultati

Tablica 2. pokazuje glavne vrijednosti stupnja konverzije i standardne devijacije ($p < 0,05$) hibridnih i kompozitnih materijala s mikropunilom rabljenih u ovom eksperimentu. Sve vrijednosti dobivene pulsnim laserom znatno su veće od onih ostvarenih halogenom žaruljom (Heliolux GTE) za sve rabljene materijale i boje. Vrijednosti variraju od

Tablica 2. Srednje vrijednosti i standardne devijacije za svijetlu i tamnu boju kompozita osvijetljenih dvjema polimerizacijakim tehnikama

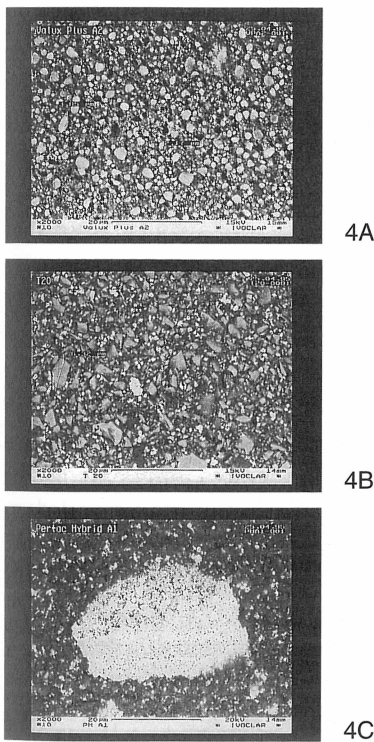
Table 2. Mean values and standard deviations for light and dark shades of different composites polymerized by two polymerization methods

STUPANJ KONVERZIJE % srednje vrijednosti i standardne devijacije DEGREE OF CONVERSION (%) mean values and standard deviations ($p < 0.05$)						
	Tehnika polimerizacije pulsnim laserom Pulsed laser polymerization technique			Heliolux GTE		
	\bar{x} surface	\bar{x} 1,0 mm	\bar{x} 2,0 mm	\bar{x} surface	\bar{x} 1,0 mm	\bar{x} 2,0 mm
VPA2	84,3±2,04	86,2±2,19	81,9±4,42	72,3±0,55	72,8±0,91	71,3±2,06
VPCG	75,1±1,55	73,1±0,87	72,1±0,47	69,1±0,32	68,7±0,95	63,8±3,03
T20	83,75±0,37	82,90±0,26	82,52±0,48	69,44±0,35	68,82±1,76	66,72±4,40
T24	81,93±1,62	81,32±0,60	80,85±0,81	66,21±0,49	65,33±0,83	63,19±0,55
PHA1	73,56±4,80	70,13±5,02	71,27±1,74	68,66±3,94	63,68±2,46	63,54±0,80
PHA4	62,98±4,10	66,36±0,55	64,93±4,22	64,21±2,36	60,32±2,15	51,77±4,40
HM20	80,89±0,49	79,09±1,08	79,78±3,01	66,53±3,22	65,71±4,22	65,24±3,80
HM24	81,64±3,42	75,61±1,27	78,57±2,65	64,57±1,64	60,19±1,18	58,30±0,67
HP20	79,26±0,92	78,71±0,81	77,53±0,22	62,67±2,96	61,04±0,16	57,02±4,14
HP24	75,94±0,73	74,01±0,41	73,24±1,02	57,11±0,71	52,11±0,67	44,09±2,43
VDL	65,4±2,92	69,4±3,50	78,4±3,60	53,0±2,59	50,5±0,21	52,6±3,46
VDB	59,8±0,06	60,5±1,48	60,5±0,71	47,6±1,18	47,6±1,42	46,4±1,00



Slika 3. Polimerizacijsko skupljanje uzoraka kompozitnih materijala pri iluminaciji pulsnim laserom i Heliolux GTE halogenom žaruljom

Figure 3. Polymerization shrinkage of composite material samples illuminated by pulsed laser and Heliolux GTE curing unit



Slika 4. A) SEM slika veličine i distribucije čestica u VPA2
B) SEM slika veličine i distribucije čestica u T20
C) SEM slika veličine i distribucije čestica u PHA1

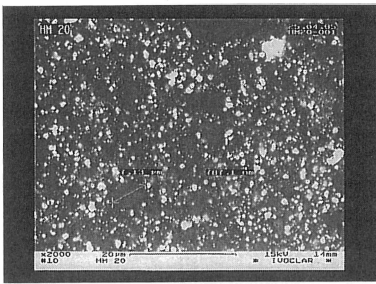
Figure 4. A) SEM picture of filler particle size and distribution in VPA2
B) SEM picture of filler particle size and distribution in T20
C) SEM picture of filler particle size and distribution in PHA1

59,8±0,06 (VDB, površina) do 86,2±2,19 (VPA2, 1,0 mm dubine) u slučaju polimerizacije pulsnim laserom i od 44,1±2,43 (HP24, 2,0 mm dubine) do 72,8±0,91 (VPA2, 1,0 mm dubine) pri uporabi halogene žarulje. U slučaju polimerizacije plavim pulsnim laserom nije bilo statistički značajne razlike između površine te dubina od 1,0 mm i 2,0 mm.

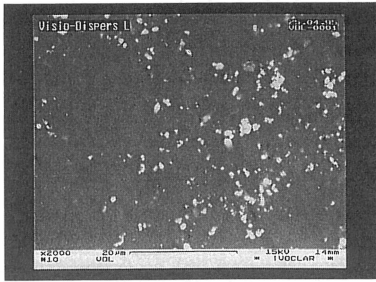
Slika 3. prikazuje vrijednosti polimerizacijskog skupljanja ispitivanih materijala. Nakon 40 s iluminacije halogenom žaruljom, 0,2 g teški kompozitni uzorci bili su nedostavno osvijetljeni zbog debljine te je bilo nužno produžiti vrijeme polimerizacije na 120 s kako bi se ostvario stupanj konverzije usporedio s vrijednostima dobivenim iluminacijom pulsnim laserom nakon 40 s. Rezultati polimerizacijskoga skupljanja niži su kod iluminacije pulsnim laserom za sve rabljene materijale i boje nego pri iluminaciji halogenom žaruljom nakon 120 s. Vrijednosti polimerizacijskog skupljanja kreću se od 0,8±0,06% do 3,2±1,10% u slučaju iluminacije pulsnim laserom, a u slučaju polimerizacije halogenom žaruljom od 2,5±0,40% do 4,1±0,42%.

Slika 4. A-C pokazuje SEM snimke triju različitih hibridnih kompozita (VP, T i PH) pri povećanju 2000x. Veličina i distribucija čestica punila raščlanjeni su uporabom kompozicijskoga kontrasta sa sekundarno raspršenim elektronima.

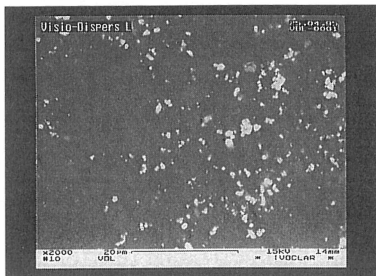
Slika 5. A-C prikazuje tri različita kompozita s mikropunilom (HM, HP, VD) pri istom povećanju



5A



5B

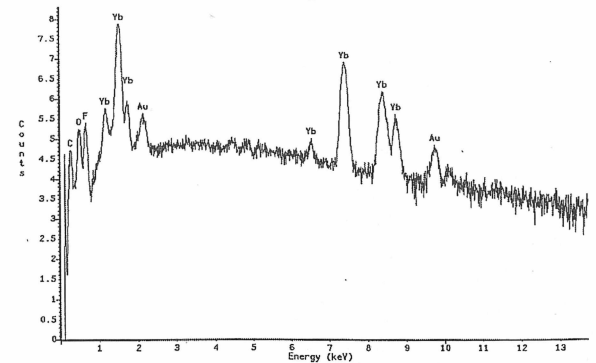
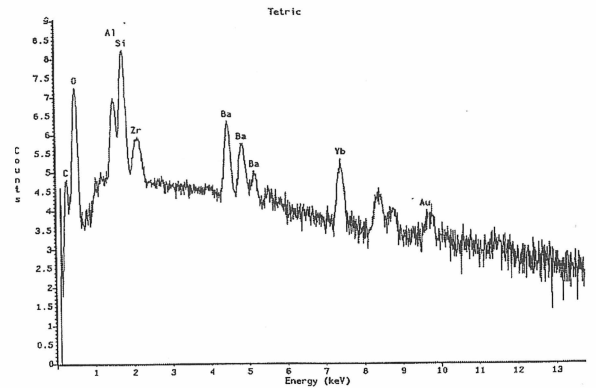


5C

Slika 5. A) SEM slika veličine i distribucije čestica u HM20
B) SEM slika veličine i distribucije čestica u HP20
C) SEM slika veličine i distribucije čestica u VDL

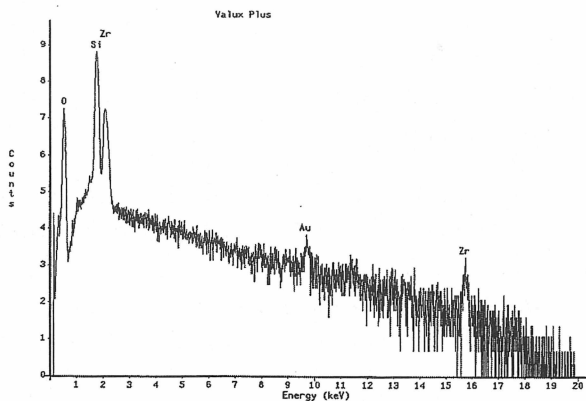
Figure 5. A) SEM picture of filler particle size and distribution in HM20
B) SEM picture of filler particle size and distribution in HP20
C) SEM picture of filler particle size and distribution in VDL

u i prije spomenutoj tehnici. Slike 6, 7 i 8 prikazuju mikrorasčlambu energetski dispergiranih X-zraka rabljenu za određivanje vrste čestica punila kod hibridnih kompozitnih materijala. Razlika u sastavu materijala može biti uzrokom za statistički niže vrijednosti kod kompozitnih materijala s mikropunilom.



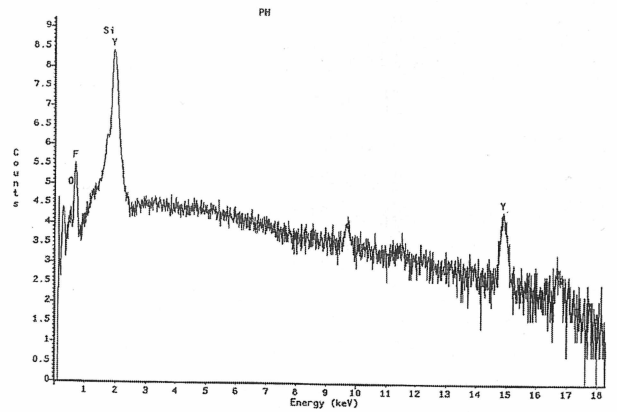
Slika 7. SEM mikrorasčlamba energetski dispergiranih X-zraka kod Tetrica

Figure 7. SEM Energy-dispersive X-ray microanalysis of Tetric



Slika 6. SEM mikrorasčlamba energetski dispergiranih X-zraka kod Valux Plusa

Figure 6. SEM Energy-dispersive X-ray microanalysis of Valux Plus



Slika 8. SEM mikrorasčlamba energetski dispergiranih X-zraka kod Pertac Hybrid

Figure 8. SEM Energy-dispersive X-ray microanalysis of Pertac Hybrid

Rasprava

U standardnim uvjetima polimerizacije veći stupanj konverzije rezultira i većim polimerizacijskim skupljanjem (14). Zadovoljavajući kompozitni ispun trebao bi ostvariti uz dostatan stupanj konverzije, i minimalno polimerizacijsko skupljanje.

Dobiveni rezultati pokazuju da su ispitivani parametri polimerizacije kompozita bolji u slučaju uporabe pulsnoga lasera za sve promatrane materijale (hibridne i one s mikropunilom) i boje (svijetle i tamne) u usporedbi sa standardnom tehnikom. Također je važno da postoji statistički znatna razlika između svijetlih i tamnih boja kompozitnih materijala stvrdnutih pulsnim laserom odnosno halogenom žaruljom. Za bolju interpretaciju promatranih rezultata rabljena je SEM raščlamba vrste, veličine i distribucije čestica punila. Vrijednosti stupnja konverzije veće su na površini nego na dubini 1,0 i 2,0 mm u slučaju osvjetljavanja halogenom žaruljom (15), a u slučaju polimerizacije pulsnim laserom nije utvrđena statistički značajna razlika između površine i dna uzorka. Bilo je i rezultata, kod iluminacije pulsnim laserom, kod kojih je ustanovljen veći stupanj konverzije u dubljim slojevima nego na površini (VPA2, PHA1, PHA4, HM24, VDL i VDB), što može značiti samo devijaciju mjerenja. Za konvencionalnu halogenu svjetiljku Heliolux GTE (500 mW/cm²) ustanovljene su niže vrijednosti konverzije u dubljim slojevima u 9 od 12 testiranih materijala.

Poznato je da su svjetiljke visokog intenziteta (>233 mW/cm²) široko preporučene za adekvatnu polimerizaciju. No, one imaju loš utjecaj na spoj zub-kompozitni materijal osobito u kavitetima s visokim C-faktorom. U kliničkim uvjetima, gdje je nemoguć tijesan dodir uređaja za polimerizaciju i površine ispuna, ne može se žaruljama s visokim intenzitetom postići odgovarajući stupanj konverzije. Za takve situacije isti stupanj konverzije na površini i u dubini može se postići iluminacijom pulsnim laserom.

Dubina stvrdnjavanja rezultat je intenziteta svjetla koji opada s debljinom uzorka limitirajući tako maksimalan doseg polimerizacijske reakcije. Međutim, temperatura koja povećava stupanj konverzije ujedno povećava i polimerizacijsko skupljanje. Pojačanja, punila i pigmenti utječu na prodor svjetla ograničavajući dubinu stvrdnjavanja.

McCabe i Carick (16) utvrdili su da intenzitet izvora svjetla, njegova apsorpcija i raspršenje u materijalu utječu na konverziju. Transmisija svjetla važan je čimbenik za postizanje veće dubine stvrdnjavanja. Kod tamnih i više opaknih boja za očekivati je manji transmisijski koeficijent i manji stupanj konverzije. Apсорpcija svjetla uvelike je ovisna o pigmentu materijala. Žuti pigment apsorpira više plavoga svjetla, što inducira polimerizaciju (17).

Rezultati pokazuju niže vrijednosti stupnja konverzije za kompozitne materijale s mikropunilom. Kako je pokazano u nekoliko studija (18,19), prodor i raspršivanje svjetla povezano je s veličinom čestica punila u materijalu. Prema Ruyteru i Øysaedu rasap svjetla je maksimalan kada su čestice punila 1/2 valne duljine aktiviranoga svjetla. Količina SiO₂ čestica mikropunila iznosi 0,04 μm (20). Aglomerati čestica koji odgovaraju 1/2 valne duljine (λ=450-500 nm) veličine su oko 0,25 μm. Zato se razmjerno niža dubina stvrdnjavanja kompozitnih smola s mikropunilom može objasniti aglomeratima čestica punila kritične veličine.

Hibridni kompoziti pokazuju veći stupanj konverzije monomera nego oni s mikropunilom. No, ispitivani hibridni kompozitni materijal PH dao je niže rezultate nego druga dva hibridna materijala. Slika 4 A i B (VP i T) pokazuju ravnomjernu distribuciju čestica punila približno sličnog oblika i razlikuju se od PH (Slika 4 C) gdje se može opaziti nepravilan raspored čestica punila s velikim česticama kvarca.

Niži rezultati polimerizacijskog skupljanja ustanovljeni su pri polimerizaciji pulsnim laserom. Naime, osvjetljavanje pulsnim laserom omogućuje veći stupanj konverzije i reducira polimerizacijsko skupljanje. Radeći ispitivanje s pulsnim laserom, nitko nije očekivao ovakvu razliku volumetrijskih promjena kompozitnih uzoraka u usporedbi s iluminacijom s pomoću kontinuiranoga lasera (12,21). Postoji znatna razlika u mehanizmu stvrdnjavanja između standardne halogene žarulje i kontinuiranog emitiranja lasera s jedne strane te pulsnog lasera s druge strane. Pulsni laser daje koherentni snop svjetlosti, tj. svi su fotoni vremenski i prostorno sjeđinjeni. Zbog monokromatskoga svjetla pulsnoga lasera, koji odgovara maksimumu apsorpcijske krivulje kamforinona (468 nm) i prodornosti laserskog nanopulsa, za očekivati je manje opadanje intenziteta svjetla zbog saturacijskog učinka u dubi-

ni kompozita, što rezultira većim dosegom konverzije monomera.

Manje polimerizacijsko skupljanje i veći stupanj konverzije monomera može biti ostvaren s čak pet puta manjom energijom nego kod standardne halogene žarulje (23). U ovom eksperimentu količina energije osvjetljenih uzoraka bila je 4 J pri uporabi pulsnoga lasera u usporedbi s 20 J pri ilimnaciji halogenom žaruljom. Kratki (20 ns), ali oštri nanopulsevi omogućuju relaksaciju materijala u razdoblju hlađenja (0,1 s) između laserskih pulseva, reducirajući time porast temperature u uzorku i kao posljedicu toga polimerizacijsko skupljanje materijala.

Zaključak

1. Utvrđene su statistički veće vrijednosti stupnja konverzije za sve ispitivane materijale bez obzira na vrstu i boju materijala pri uporabi pulsnoga lasera.
2. U slučaju osvjetljavanja pulsnim plavim laserom nije bilo statistički značajne razlike u stupnju konverzije između površine uzorka te dubina od 1,0 mm i 2,0 mm.
3. Statistički značajno smanjenje polimerizacijskoga skupljanja opaženo je kod polimerizacije pulsnim plavim laserom u usporedbi s konvencionalnom halogenom žaruljom.

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Some Properties of Composite Resins Cured by Pulsed Blue Laser

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Summary

The purpose of the study was to analyse some properties of composite resin samples cured by pulsed laser in comparison with standard halogen light. Three hybrid and three microfilled commercial composite materials were polymerized in the experimental conditions using an excimer laser pumped dye laser (XeCl Lambda Physik LPX 100/LPD 3002) and a standard curing unit (Heliolux GTE). The samples were spectroscopically analysed (FTIR) for the degree of conversion, scanning electron microscopy (SEM) was performed for characterising the structure of the material, and volumetric shrinkage behaviour was tested using density bottle method. Statistical analysis of the data (ANOVA $p < 0.05$) shows that the degree of conversion values obtained by excimer laser was significantly higher for all the materials and shades tested while the polymerization shrinkage values were significantly lower compared with the conventional curing unit. Those results are clinically very important in situations whenever close approximation of the light curing tip to the composite surface is impossible. The monochromatic pulsed dye laser set at 468 nm allows high penetration into the sample and the nature of the pulse allows homogenous high quality curing with decreased shrinkage of the composite resin. The sensitivity of the tooth after the placement of direct composite restoration is mainly connected with the polymerization contraction. Adhesive and cohesive fractures appear in dentin, hybrid layer and material itself. The amount of volumetric increase is in accordance with the degree of cure, the type of composite material and the nature of the activating light.

Key words: *composite resins, laser, monomer conversion, polymerization shrinkage*

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Introduction

Existing types of photocurable composites exhibit polymerization shrinkage of monomers during the setting process causing adhesive and cohesive failure and interfacial gap formation between material and tooth structure (1). The objective of obtaining optimal material properties of composite filling conflicts with achieving optimal integrity of the composite-cavity interface (2). Several approaches have been used to overcome antagonism between the degree of conversion and the polymerization shrinkage and to reduce the stress such as the use of dentin bonding agents or stress absorbing lining materials. However, when strong bonds are obtained, the solubility of dentin or the connection between the hybrid layer and the underlying dentin may be the limiting factor for the strength of such bonds (3).

Stress development in bonded composite restorations depends on the restoration geometry, in that the pregelation flow of the material is inhibited when the ratio of the bonded surface to the free unbonded surfaces exceeds a certain limit (4,5). Further approach is the use of low intensity halogen light curing units to control the flow capacity of the restoration during polymerization, although it could be a particularly significant problem whenever close approximation of the curing tip is impossible (6,7). Progress towards elimination of polymerization shrinkage by synthesis of monomers that expand upon polymerization has been reported (8-11), but such a monomer system has not yet been incorporated into commercial dental materials.

The purpose of this study was to compare standard and pulsed dye laser polymerization of different hybrid and microfilled composite samples by determining:

- degree of conversion of composite samples using Fourier transform infrared spectroscopy (FTIR);
- size, type, distribution and filler weight percentage of particular composite by scanning electron microscopy (SEM);
- polymerization shrinkage (Density bottle method).

Materials and methods

The hybrid and microfilled composite materials used in this study, are presented in Table I. A pul-

sed laser, used as the light source for photopolymerization, consisted of an excimer laser (XeCl Lambda Physik LPX 100, Göttingen, Germany) and dye laser (Lambda Physik 3002, Göttingen, Germany) with Coumarin 102 dye. The laser pulse duration was 20 ns, the total number of pulses was 400 with repetition rate of 10 Hz (Figure 1), the energy of 10 mJ per pulse and the wavelength 468 nm. The control measurement was performed using a Helio-lux GTE (Ivoclar/Vivadent, Schaan, Liechtenstein) curing unit of 500 mW/cm² output, measured by a Curing Radiometer Model 100 (Demetron Research Corporation, Danbury, CT, USA). Composite resin samples were prepared in the same way for experimental and control polymerization methods as already described (12). The composite resin samples were prepared in the same way for the standard halogen lamp and for the pulsed laser illumination. The intention was to simulate composite resin wafer on the surface and at 1.0 mm and 2.0 mm depths, using 1.0 mm and 2.0 mm thick overlays, previously cured in Spectramat PM 1831 (Ivoclar/Vivadent, Schaan, Liechtenstein) two minutes each side to a high degree of conversion. Underlays of the same thickness were made from the same material to ensure constant backing reflectance. A thin wafer of uncured composite was placed between two Mylar sheets and pressed by 100 bar to a 0.1 mm thickness. For surface measurements, an uncured sample was placed between two Mylar sheets and illuminated for 40 seconds, while for the measurements at deeper depth, the cured overlay was placed above the upper Mylar sheet and fiber optic tip was attached to the overlay and again illuminated for 40 seconds. In case of pulsed laser illumination the composite resin sample was fixed to the metal holder, and so were the overlay and underlay when simulating the wafer at a particular depth. The laser beam passed through the divergent lens and came dispersed upon 1 cm² of the sample surface. The exposition time was again 40 seconds.

Degree of conversion measurements

The FTIR spectra of the cured samples were recorded in transmission mode at room temperature using a Perkin Elmer Spectrometer, model 2000, in the IR region 4000-400 cm⁻¹ (Perkin Elmer, Beaconsfield, Bucks, England). The spectrometer was

coupled with an IR Data Manager (IRDM) program. Uncured samples were pressed into KBr discs. Spectroscopically pure KBr supplied by Merck (Darmstadt, Germany) was used. The spectra were collected with 20 scans at a resolution of 4 cm⁻¹. The peak ratios were calculated according to Rueggeberg's baseline method (13). The degree of conversion was calculated from the equivalent aliphatic (1638 cm⁻¹) / aromatic (1610 cm⁻¹) molar ratio of cured (C) and uncured (U) samples using the formula proposed in the same article: % conversion = (1-C/U) x 100.

Scanning Electron Microscopy

Disc shaped composite resin samples, 1 mm thick and 25 mm in diameter, were gold coated and examined by Digital Scanning Microscope - DSM 962 (Zeiss, Jena, Germany). Filler particle distribution was analysed by Compositional contrast with secondary backscattered electrons. Energy-dispersive X-ray microanalysis was used to determine filler particles type for hybrid composite materials.

Polymerization shrinkage measurements

The polymerization shrinkage of the specimens investigated in the present study was determined by the density bottle method. A Sauter balance with accuracy of + 0.00001 g (August Sauter KG, Ebingen, Germany) was used and measurements were performed at room temperature. Cylindrically shaped specimens of approximately 0.2 g in weight were placed in a density bottle of 20 cm³ volume containing water (q_{H₂O} at 25 °C = 0.99707 g/cm³). Shape and size of the mould used for specimen preparation is presented in Figure 2. Specimens were illuminated by standard halogen lamp or pulsed laser before measurements for 40" and 120", respectively. Each specimen was tested on three successive occasions. Density of the specimen was calculated according to the equation:

$$q = ((C-A)/((B-A)-(E-C))) \times q_{H_2O} \text{ (q/cm}^3\text{)}$$

q = density of material

A = weight of density bottle

B = weight of density bottle + water

C = weight of density bottle + specimen

E = weight of density bottle + specimen + water

The change in density between the uncured and cured specimen serves to calculate its volume contraction, i.e. shrinkage. Shrinkage percentage S (%) was then calculated as follows: $S = (1 - q_N/q_p) \times 100$; where q represents the density of uncured and cured material in g/cm³.

The degree of conversion and polymerization shrinkage values were analysed by one-way and three-way analysis of variance (p<0.05). Statistical SPSS packet was used for graphical representation of polymerization shrinkage results.

Results

Table II shows the degree of conversion mean values and standard deviations (p<0.05) of the hybrid and microfilled composites used in this experiment. All values obtained by pulsed laser were significantly higher than those obtained by conventional unit (Heliolux GTE) for all the materials and shades observed. These values varied from 59.8 ± 0.06 (VDB, surface) to 86.2±2.19 (VPA2, 1.0 mm depth) in the case of pulsed laser polymerization and from 44.1 ± 2.43 (HP24, 2.0 mm depth) to 72.8 ± 0.91 (VPA2, 1.0 mm depth) when standard halogen lamp was used. In the case of pulsed blue laser polymerization there was no statistically significant difference between the surface and the depth of 1.0 mm and 2.0 mm.

Figure 3 presents polymerization shrinkage values. After 40 s. of standard illumination, composite samples were insufficiently cured due to the required thickness, and it was necessary to prolong the polymerization time to 120 s. to provide the degree of conversion comparable to the values obtained after 40 sec pulsed laser illumination. Polymerization shrinkage values were significantly lower in the case of pulsed laser for all the materials and all the shades observed than in 120 s. halogen light curing. The polymerization shrinkage values varied from 0.8±0.06% to 3.2 ± 1.10% in the case of pulsed laser illumination while in the case of standard they were between 2.5 ± 0.40% and 4.1 ± 0.42%.

Figure 4 A-C shows SEM pictures of three different hybrid composites (VP, T and PH) using 2000 X magnification. Filler particle size and distribution were analysed using Compositional contrast with secondary backscattered electrons. Figure 5 A-C shows three different microfilled composites (HM, HP and VD) analysed at the same magnification, using the previously mentioned technique. Figures 6, 7 and 8 present Energy-dispersive X-ray microanalysis used to determine filler particle type for hybrid composite materials. The difference in the composition of the materials may be responsible for the significantly lower values of microfilled composite materials.

Discussion

In standard photopolymerization conditions a higher degree of conversion leads to higher polymerization shrinkage values (14). However, appropriate composite resin filling requires a sufficient degree of conversion and minimal polymerization shrinkage. The results obtained revealed that the tested parameters of composite polymerization were more successful in the case of pulsed laser polymerization for all materials (hybrid and microfilled) and shades (light and dark) observed compared with the standard technique. It is also very important that there was statistical difference between the light and dark shades of composites, illuminated by pulsed laser or by standard halogen lamp.

For better interpretation of the obtained results, SEM analyses of filler particle type, size and distribution was performed. The degree of conversion mean values were significantly higher on the surface than at depths of 1.0 and 2.0 mm in the case of standard curing (15), while in the case of pulsed laser polymerization no essential difference was observed between the top surface and the bottom of the sample. There were even some results where in the case of pulsed laser illumination a higher degree of conversion values was obtained in the deeper layers than on the surface (VPA2, PHA1, PHA4, HM24, VDL and VDB), which could mean merely deviations of the measurements. For the conventional curing high intensity Heliolux GTE was used (500 mW/cm²) and significantly lower conversion values were obtained in the deeper layers for 9 out of 12 materials tested. It is well known that high

intensity lamps (>233 mW/cm²) are widely recommended for adequate polymerization. However, they have a bad effect on the composite-cavity interface especially in cavities with high C-factor. There are clinical situations where close approximation of the curing tip is impossible and low intensity curing lamps cannot ensure a satisfactory degree of polymerization. For such situations the same conversion rate obtained on the top surface and in the deeper layers, in the case of pulsed laser illumination, is very important.

The depth of cure is a result of the light intensity that decreases with the thickness of the sample limiting the maximum degree of the reaction. However, the temperature that increases the maximal degree of conversion, also increases the polymerization shrinkage. Reinforcements, fillers and pigments strongly influence the intensity of the incident light, limiting the depth of cure.

McCabe and Carrick(16) reported that both intensity of the light source and attenuating power of the material influence conversion. Light transmission is an important factor in achieving greater curing depth. Darker and more opaque shades might be expected to have lower transmission coefficient and a lower degree of conversion values. Absorption is greatly influenced by material pigmentation. Yellow pigment absorbs more blue light which induces polymerization (17).

The results revealed smaller conversion values for microfilled composites. As has been shown by several researchers (18,19), light scattering is related to filler particle size in the material. Ruyter and Øysaed have suggested that light scattering is maximised when the filler particle size is one-half the wavelength of activation light. The average SiO₂ particle of microfillers was reported as 0.04 µm (20). The agglomerated particle size that corresponds to one-half the wavelength ($\lambda=450-500\text{nm}$) is about 0.25 µm. Thus, the relatively lower cure depth of microfilled composites could be explained due to the agglomerated filler particles of critical size.

Hybrid composites ensured higher monomer conversion than microfilled composites. However, tested conventional hybrid material PH produced slightly lower values than two other hybrid materials. Figure 4 A and B (VP and T) show regular distribution of similarly shaped filler particles and differ from PH (Figure 4 C) where irregular filler particle

distribution with a big quartz particle can be observed.

Significantly lower polymerization shrinkage values were obtained in the case of pulsed laser polymerization. Namely, pulsed laser curing enables a higher degree of conversion and reduced polymerization shrinkage. Starting the experiment with pulsed laser such a difference regarding volumetric behaviour of the composite sample in comparison with continuous laser illumination was not expected (12,21). There is a significant difference in curing mechanism between standard halogen curing unit and continuous wave laser on the one hand and pulsed laser of the same colour on the other. Pulsed laser light is coherent, i.e. all the photons are in temporal and spatial coherence. Because of the monochromaticity of the pulsed laser light, set at a maximum of camphorquinone absorption curve (468 nm), and much greater intensity of the laser pulse, one would expect less attenuation due to the laser saturation effect in the depth of composite, thus resulting in a greater extent of monomer conversion (22).

Lower polymerization shrinkage and higher monomer conversion values could be obtained with even 5 times less energy than in standard halogen light curing (23). In this experiment, the amount of

energy illuminating the sample surface was 4 J, when using pulsed laser compared to 20 J illuminating the sample surface in the case of the standard polymerization method. Short (20 ns) but very piercing nanopulses allow relaxation of the material in the cooling period (0.1 s) between the laser pulses, thus reducing the temperature rise in the sample and consequently polymerization shrinkage of the material.

Conclusions

1. A significantly higher degree of polymerization values for all the composites tested, regardless of the type and shade of the material, were obtained when pulsed laser photopolymerization technique was used.
2. In the case of pulsed blue laser curing there was no statistically significant difference in the degree of polymerization between the top surface and the depth of 1.0 mm or 2.0 mm.
3. Significantly reduced polymerization shrinkage values were obtained when a pulsed blue laser was used compared to a conventional curing halogen lamp.