Possible Improvements
of Clinical Properties of Dental Composite Materials
with Pulsed Blue Laser Curing

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Despite considerable improvements of dental composite materials, the present-day composite resins still suffer from two major shortcomings that limit their use: inadequate degree of conversion and polymerization shrinkage. The objective of this study was to evaluate the degree of conversion and polymerization shrinkage of two hybrid and two microfilled composite materials cured by pulsed blue dye laser pumped XeCl excimer laser at 308 nm and the standard curing unit. The degree of conversion was measured by a Perkin Elmer FTIR spectrometer at the surface of the material and at a 3.0 mm depth. Statistical analysis (ANOVA $p < 0.05$) showed a significantly higher degree of conversion values in the case of pulsed laser. Polymerization shrinkage measured by a pycnometer showed significantly lower values in the case of pulsed laser curing for six out of eight materials observed. The saturation effect in the material illuminated by monochromatic blue pulsed laser light (468 nm) may be responsible for the higher degree of conversion, while the relaxation of the molecules between nanopulses may lead to a reduced polymerization shrinkage.

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INTRODUCTION

The effectiveness of polymerization in dental composite resins depends on the chemistry of the material, initiator concentration, filler particle type, size and quantity as well as on the effectiveness of the radiation source for the matching absorption curve of camphorquinone, intensity, irradiation time and alignment of the light tip guide.[1,2]

Polymerization shrinkage occurs when the composite restorative material is cured. The degree of shrinkage of a composite is related to the molecular weight of the monomer, the amount of monomer in the composite and the degree of conversion.[3] Hence, the objective of obtaining optimal material properties conflicts with the objective of achieving optimal integrity of the composite-cavity interface.[4] In an ideal situation, the degree of conversion of a restorative resin should be the same throughout its depth. However this is never the case. It has been suggested that the lower and upper hardness surface gradients should not exceed 10–20% for adequately cured resin composites.[1] Both factors highly influence the quality of composite resin filling, and considerable efforts are being made world-wide to reduce or eliminate these undesirable properties.[5] There are several methods of counteracting shrinkage and the resulting stresses, such as utilizing more adhesive bonding agents, elastic »stress absorbing« lining materials, decreasing the curing light intensity, incremental placement techniques, the use of potentially low-shrinking or non-shrinking dental monomers and the use of fluoride-releasing monomer systems to mitigate the negative effects of marginal gaps.[6,7] However, all of these approaches to reducing stress at the composite-cavity interface have some unavoidable disadvantages. Modern adhesives have a high bond strength value, but polymerization shrinkage stresses have a potential to initiate adhesive failure of the composite-tooth interface, which may cause microleakage and secondary caries or initiate microcracking of the restoration material or deformation of the tooth (cohesive failure). The use of »stress absorbing« lining materials is unnecessary in shallow cavities. The third approach aimed at enhancing the restoration cavity integrity is the use of a light curing unit of lower intensity.[8] However, the effect of light intensity and exposure duration play a major role when it comes to illuminating the composite resin of dark shades in the undercuts and deeper cavities or whenever close approximation of the fiber optic tip is impossible. Recent analyses have shown that in restoration with a well established bond to the tooth, incremental filling techniques increase deformation of the restored tooth.[9,10] The latest approach to counteract polymerization shrinkage is the use of new expanding dental monomers, but such systems have not yet been completely incorporated into commercial dental materials.[11] Two other solutions, the one being »softstart polymerization« where the light initiated prepolymerization at low intensity, followed by a post-light-cure at full intensity, may lead to light-cured composite fillings with improved marginal adaptation.[12] Also, extra-orally cured inlay/on-

lay materials, where the polymerization reaction is initiated and completed in an oven and all the shrinkage occurs before the cementation, exhibited less marginal degradation and reduced postoperative sensitivity in comparison with direct composite restoration.[13–16]

In the present study, the aim was to investigate whether an optimal degree of conversion of the composite resin and minimal polymerization shrinkage could be obtained using a pulsed blue excimer laser as a new light source.

EXPERIMENTAL

Hybrid and microfilled composite materials, used in this experiment, are presented in Table I. Light and dark shades have been examined for both types of material.

Light Sources

A pulsed blue laser, used as a new light source for photopolymerization, consisted of an excimer laser (XeCl Lambda Physik LPX 100), pumped dye laser (Lambda Physik 3002) with Coumarin 102 dye.[17] The wavelength was set at 468 nm, where the maximum of the camphorquinine absorption coefficient is located. The laser pulse duration at half a maximum was 20 ns, the total number of pulses was 400 with a repetition rate of 10 Hz and energy of 10 mJ per pulse. Control measurement was performed using a Heliolux GTE (Ivoclar/Vivadent, Schaan, Liechtenstein) curing unit of 500 mW/cm^2 output, measured by a Curing Radiometer Model 100 (Demetron Research Corporation, Danbury, CT, USA).

Specimen Preparation

The intention was to simulate a composite resin wafer at the surface and at the depth of 3.0 mm.[18] To ensure this, 3.0 mm thick overlays as well as underlays, previously cured in a Spectramat PM 1831 (Ivoclar/Vivadent, Schaan, Liechtenstein), were used. The samples were recorded by pressing (10^7 Pa) a thin layer of uncured composite, placed between two mylar sheets, to a 0.2 mm thickness and polymerized for 40 seconds for surface measurements. In cases of simulating the composite resin wafer at a particular depth, the cured overlay of appropriate thickness was placed above the upper mylar sheet and the fiber optic tip pressed onto the overlay also for 40 seconds. In cases of pulsed laser illumination, the laser beam passed through a divergent lens and illuminated 1 cm^2 of sample surface, at a distance of 5.0 mm from the lens. For both photopolymerization techniques, three independent measurements on three specimens of the same material were performed. Cured samples were stored in a dark environment at 37 °C for 24 hours.

Degree of Conversion Measurements

Cured and uncured specimens were measured by Fourier Transform Infrared Spectroscopy (FTIR Spectroscopy). Cured specimens were separated from mylar sheets while the uncured ones were pressed into KBr pellets with a Carver press (Perkin Elmer). Spectroscopically pure KBr was used (Merck, Darmstadt, Germany).

TABLE I

Composite materials used in the experiment

COMPOSITE	MANUFACTURER	SHADE	ABBREVIATION
Tetric	Vivadent (Schaan, Liechtenstein)	light	T20
Tetric	Vivadent (Schaan, Liechtenstein)	dark	T24
Valux Plus	3M Dental Products (St. Paul. MN)	light	VPA2
Valux Plus	3M Dental Products (St. Paul. MN)	dark	VPCG
Helioprogress	Vivadent (Schaan, Liechtenstein)	light	HP20
Helioprogress	Vivadent (Schaan, Liechtenstein)	dark	HP24
Visiodispers	ESPE (Seefeld, Germany)	light	VDL
Visiodispers	ESPE (Seefeld, Germany)	dark	VDB

The IR spectra were scanned at room temperature in a transmission mode using a Perkin Elmer 2000 spectrometer (Perkin Elmer, Beaconsfield, Buchs, England). Spectral conditions consisted of a 4 cm $^{-1}$ resolution and 20 scans. An· IR Data Manager (IRDM) program for numerical evaluation of the spectra was used. The peak ratios were calculated according to Rueggeberg's baseline method. The degree of conversion was calculated from the equivalent aliphatic (1638 cm^{-1}) / aromatic (1610 cm^{-1}) molar ratios of cured (C) and uncured (U) samples using the formula proposed in the literature:[19] % conversion = (1–C/U) x 100%

Polymerization Shrinkage Measurements

The polymerization shrinkage of cured and uncured specimens tested in the present study was determined by the density bottle method, at room temperature. The specimens in the form of small cylinders (approximately 0.2 g in weight) were placed in a density bottle of 20 cm^3 volume containing redistilled water (q_{H20} at 25 °C = 0.99707 g/cm^3). A Sauter balance (accuracy = ± 0.00001 g) manufactured by August Sauter KG, Ebingen, Germany, was used. Three successive measurements for all tested composites were performed. Material density was calculated using the equation:

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

where q = material density, A = density bottle weight, B = density bottle weight + water, C density bottle weight + specimen, and E = density bottle weight + specimen + water.

The percentage of polymerization shrinkage S (%) was then calculated according to the equation:

$$S = (1 - q_u/q_c) \times 100$$

q_u = density of uncured material (g/cm^3) and q_c = density of cured material (g/cm^3).

The degree of conversion and polymerization shrinkage values were analyzed by the one-way and three-way analysis of variance ($p < 0.05$).

RESULTS AND DISCUSSION

Figure 1 shows the mean values of the degree of conversion and standard deviations of the composites used in the experiment. All values of the degree of conversion obtained by pulsed laser photopolymerization were sig-
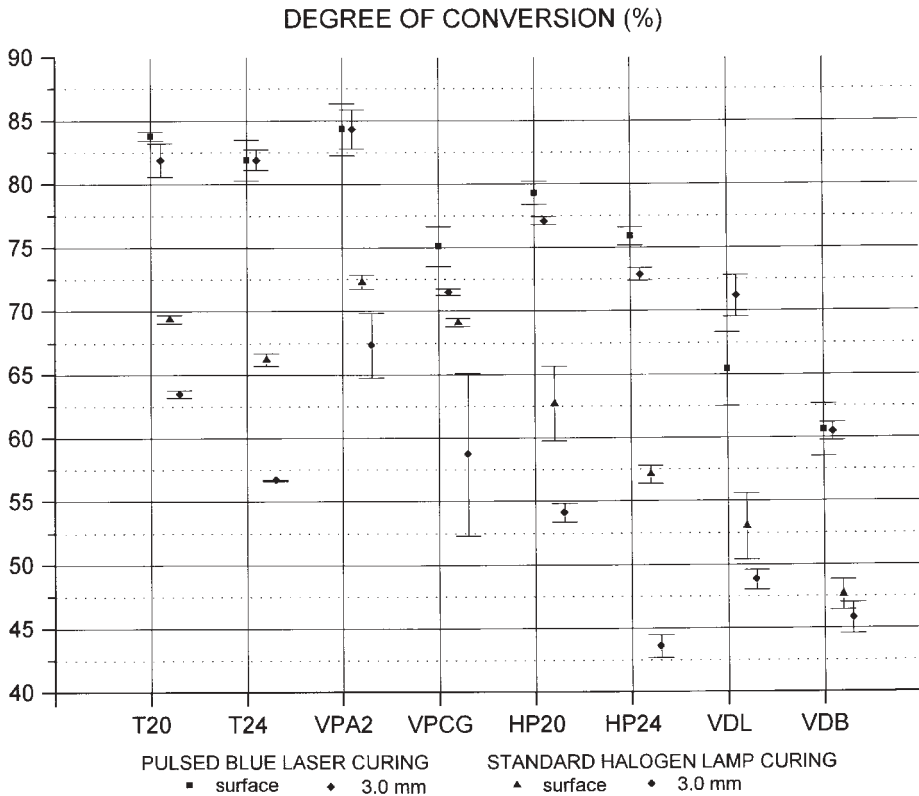

Figure 1. Degree of conversion of pulsed blue laser and standard halogen lamp cured composites.

nificantly higher than those obtained by the conventional curing unit. At both depths, the light shade of all materials reflected a higher conversion than the dark one. Generally, the degree of conversion significantly decreased at the 3.0 mm depth in the case of conventional halogen lamp curing, while in the case of pulsed laser illumination a very weak dependence on the distance from the surface was observed.

Figure 2 presents the polymerization shrinkage mean values and standard deviations.[20] The illumination time was prolonged to 120 s to provide the degree of conversion comparable to the values obtained by pulsed laser polymerization. In the case of pulsed blue laser illumination, the polymerization shrinkage values were significantly lower for six out of eight materials observed. Measurements were also performed after 40 s of Heliolux curing unit illumination but very low polymerization shrinkage values were obtained (they varied from 0.9 ± 0.20 for T24 to 2.1 ± 0.52 for VPCG). The reason for these low values is believed to be insufficient curing, *i.e.* transformation of the fluid resin into a rubber (gelation), and then into a solid glass (vitrification), as a result of chemical reactions between multifunctional groups, was interrupted in the rubbery state.[21] About 10–15% of conversion occurs during gelification. The illumination time was prolonged to 120 s to provide a degree of conversion as close as possible to the values obtained after 40 s pulsed laser illumination where the degree of conversion varied
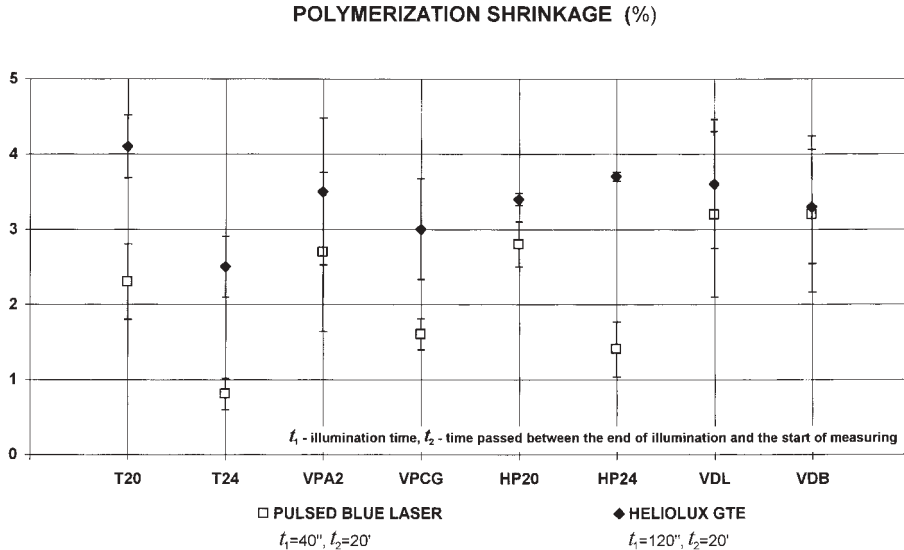
POLYMERIZATION SHRINKAGE (%)

Figure 2. Polymerization shrinkage of pulsed blue laser and standard halogen lamp cured composites t_1 Illumination time, t_2 Time elapsed between the end of illumination and the start of measuring.

from 60.5 ± 0.71 (VDB at the depth of 3.0 mm) to 84.3 ± 2.04 (VPA2 at the surface). Furthermore, the degree of reaction in light-cured composites varies within the bulk of the specimen because the rate of the reaction is dependent upon the light intensity available at different depths.[22] Reinforcements, fillers and pigments strongly reduce the intensity of the incidental light limiting the cure depth. As pointed out by Pilo and Cardash,[23] incomplete curing in the restoration bulk is analogous to a restoration composed of several different materials. A well-cured surface layer of the restoration covers incompletely the cured deeper portions and may cause bending of the outer layer, inward displacement, marginal fracture or open margins.[24] Ruggeberg and Craig[25] reported that maximal conversion was noted in specimens with little or no overlay thickness. Conversion values below 2.5 mm overlay declined at an even higher rate, with the lowest conversion (5%) noted with the 4.5 mm overlay. Incremental layer thickness should not exceed 2.0 mm, while 1 mm is ideal.[26, 27] All of the above mentioned facts motivated the use of a prolonged illumination time of the conventional curing unit to achieve an adequate cured specimen weighing approximately 0.2 g.

In standard curing, a higher degree of conversion leads to higher polymerization shrinkage values. The results obtained revealed the tested parameters of the effectiveness of polymerization to be more successful in the case of pulsed blue laser curing. The question is whether the introduction of new monomer systems or new light sources will improve the longevity of composite restoration and expand the indications for resin composites. Most of the composite properties are derived from all the three basic constituents of the material (the resin matrix, inorganic filler and coupling agent). As light passes through the bulk of the composite to cause curing, it is absorbed and scattered.[28] The light scattering is maximized when the filler particle size is one-half the wavelength (0.234 μm) of activation light, thus explaining the lower degree of conversion of microfilled materials consisting of prepolymerized particles of a critical size. These factors result in attenuation of the light intensity as it passes through the restoration bulk, resulting in insufficient curing in the depth of the material. Darker shades have a lower transmission coefficient and yellow pigment absorbs more blue light, which consequently results in lower conversion values than the light shades. In standard curing conditions, a significant difference in the polymerization effectiveness is obtained between the surface and the 3.0 mm depth. Namely, the light is absorbed or scattered by the overlying composite and fewer activated camphorquinone molecules are formed, resulting in potentially fewer free radicals.[29] Even though the top may be highly cured using a low intensity curing unit, a dramatically lower conversion may occur at the depth of 3.0 mm. It means that no layer thicker than 1.0 or 2.0 mm should be used for conventional curing.[30] Recent analyses have revealed the incremental composite restoration filling techniques to result in higher polymerization shrinkage stresses than bulk fillings, which contradicts the widely

accepted belief that an incremental filling technique should be used to decrease polymerization stresses.[9,10] However, there are many clinical situations where a bulk composite filling cannot be adequately cured at the bottom of the restoration. By the use of additives with a supposed chain transfer agent function, monomer systems have been formulated to improve the degree of conversion of methacrylate double bonds and mechanical properties.[31] Aldehyde and diketone were hypothesized to be able to increase the degree of crosslinking by reacting with methacrylate double bonds and other pendant and backbone functional groups from different polymer chains in either nucleophilic or free radical reaction.[32] Significant improvements in mechanical properties consequential to aldehyde or diketone addition have been considered indications of an enhanced degree of conversion. It seems that the use of additives with diacetyl or propanal effect, causing some 15% increase in the degree of conversion of methacrylate double bonds and some 15% increase in mechanical properties, could be a viable means of developing composites for use in stress-bearing areas.[31]

In the present study, a very weak dependence on the depth of cure between the top surface and the 3.0 mm depth was observed in the case of pulsed blue laser curing. Laser light is coherent, meaning that all the photons of the light are in spatial and temporal coherence. Further, there is monochromacity or one particular wavelength and collimation presuming no divergence of the beam. All the three laser light characteristics are very important for providing a clinical advantage in cases where curing light source cannot be brought into proximity to the resin surface. The laser cured values do not decrease with an increasing distance from the surface.[33] The most efficient wavelength of 468 nm and saturation effect in the material illuminated by pulsed blue laser light may be responsible for the increased degree of conversion. Due to the monochromatic pulsed laser light and the far greater intensity of the laser pulse, one might expect less attenuation in the composite depths, resulting in a greater extent of monomer conversion. In this experiment, the amount of pulsed laser energy was one fifth (4 J) of that used in conventional curing (20 J). The curing reaction is accompanied not only by significant variations in the material viscosity, but also by extreme heat generation due to the exothermic nature of the polymerization reaction.[21,22] Resin systems shrink during polymerization mainly because the monomer molecules are located at Van der Waals distances from one another, while in the corresponding polymer, the monomeric units are within a covalent bond distance to each other. Thus, in the polymer, atoms are closer to one another than they were in the original monomer.[31] The shrinkage that occurs in a cavity before the gel point can be compensated for by the flow of resin composite from the free surface of filling. After gelation, large stresses are built up in the filling area and, in many cases, they result in adhesive failure pulling the composite away from the cavity wall, or in cohesive failure in the resin and underlaying dentine.[34]

Polymerization shrinkage is one of the main factors determining the lifetime of composite resin restoration. This motivated a search for non-shrinking resin systems. Stansbury[35] found a potential for developing high-conversion, low-shrinking monomers. A 30% – 40% reduction in shrinkage was observed upon homopolymerization of oxybismethacrylate monomers and oligomers, as compared with dimethacrylates commonly used in dentistry. For polymerization shrinkage to be minimized, a resin must be prepared in which the monomer components can efficiently engage in the cyclopolymerization while still maintaining an adequate crosslink density in the resulting monomer. It seems that such resins with reduced, but not eliminated, polymerization shrinkage are now available in a form which is compatible with the conventional dimethacrylate monomers used in dentistry.

In the present experiment, the lower total energy illuminating the sample in the case of pulsed laser curing may be responsible for the lower polymerization shrinkage values. However, the most important factor contributing to reduced net polymerization shrinkage is a very short nanopulse train that allows the material to cool and flow between laser pulses. With pulsed laser, the energy is emitted in short bursts according to a set repetitive series of pulses. No laser energy is emitted between the pulses.[36] The thermal effects increase with increasing wavelengths.[37] Exact wavelengths exclude all the temperature side effects and use the most efficient wavelength at 468 nm. It was hypothesized that the flow capacity was affected by the mode of curing.[38]

All the above facts distinguish pulsed excimer blue laser photopolymerization from the previously used methods.

With miniaturization of components and improvement in surgery tips and delivery systems, more practitioners will use laser. Laser curing of composites and other restorative materials looks particularly promising as smaller units become available and costs are reduced.[39] The future will show whether the advent of low or even non-shrinking monomer systems associated with significantly increased conversion and mechanical properties or most effective light sources would fundamentally change the resin composites and expand their indications.

At present, clinical use of effective pulsed blue light sources is rather inconvenient. However, recent development of the blue pulsed semiconductor diode laser gives hope that the presented results may find wide clinical application in the near future.

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SAŽETAK

Moguća poboljšanja kliničkih svojstava stomatoloških kompozitnih materijala polimerizacijom pulsnim laserom

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Unatoč mnogim poboljšanjima zubarskih kompozitnih materijala, današnje kompozitne smole još uvijek posjeduju dva glavna nedostatka koji ograničuju njihovu uporabu: nedostatan stupanj konverzije i polimerizacijsko skupljanje. Svrha ovog rada bila je ispitati stupanj konverzije i polimerizacijsko skupljanje dvaju hibridnih i dvaju kompozitnih materijala s mikropunilom, polimeriziranih pulsnim ekscimerskim laserom pri 308 nm i standardnom halogenom žaruljom. Stupanj konverzije određen je FTIR spektrometrom Perkin Elmer na površini materijala i na dubini od 3.0 mm. Analizom varijancije utvrđeno je da je stupanj konverzije, u slučaju polimerizacije pulsnim laserom, značajno veći ($p < 0,05$). Polimerizacijsko skupljanje mjereno je s pomoću piknometra, a dobivene vrijednosti bile su značajno manje u slučaju iluminacije pulsnim laserom za šest od osam ispitivanih materijala. Saturacijski učinak u materijalu osvijetljenom pulsnim monokromatskim plavim svjetlom (468 nm) vjerojatno je uzrok povećanju vrijednosti konverzije, dok relaksacija molekula između nanopulseva može voditi smanjenju polimerizacijskog skupljanja.