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ORIGINAL ARTICLE

Influence of irradiation time on subsurface degree of conversion and microhardness of high-viscosity bulk-fill resin composites

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Abstract

Objectives To evaluate the influence of irradiation time on degree of conversion (DC) and microhardness of high-viscosity bulk-fill resin composites in depths up to 6 mm.

Materials and methods Four bulk-fill materials (Tetric EvoCeram Bulk Fill—TECBF; x-tra fil—XF; QuixFil—QF; SonicFill—SF) and one conventional nano-hybrid resin composite (Tetric EvoCeram—TEC) were irradiated for 10, 20, or 30 s at 1,170 mW/cm^2. DC and Knoop microhardness (KHN) were recorded after 24-h dark storage at five depths: 0.1, 2, 4, 5, and 6 mm. Data were statistically analyzed using ANOVA and Bonferroni's post-hoc test ($\alpha=0.05$).

Results With increasing bulk thickness, DC and KHN significantly decreased for TEC. TECBF and SF showed a significant decrease in DC and KHN at 4-mm depth after 10-s irradiation, but no decrease in DC after 30-s irradiation ($p>0.05$). XF and QF demonstrated no significant DC decrease at depths up to 6 mm after irradiation of at least 20 s. At 4-mm depth, all materials tested achieved at least 80 % of their maximum DC value, irrespective of irradiation time. However, at the same depth (4 mm), only XF and QF irradiated for 30 s achieved at least 80 % of their maximum KHN value.

Conclusions Regarding DC, the tested bulk-fill resin composites can be safely used up to at least 4-mm incremental thickness. However, with respect to hardness, only XF and QF achieved acceptable results at 4-mm depth with 30 s of irradiation.

Clinical relevance Minimum irradiation times stated by the manufacturers cannot be recommended for placement of high-viscosity bulk-fill materials in 4-mm increments.

Keywords Bulk-fill resin composites · Degree of conversion · Microhardness · Depth of cure · Irradiation time

Introduction

Advances in material formulation, including improved filler morphology, progress with existing dimethacrylate chemistry and novel monomer technologies may improve the shortcomings of resin composite materials [1]. However, simplification of use of resin composites has not been frequently reported during the last decade [2], though clinicians desire to perform high-quality dentistry at minimal chair time. Incremental layering techniques have long been accepted as a standard and are widely used for light-curing resin composite restorations. For years, it has been an accepted fact that to create adequately cured composite restorations with minimal polymerization shrinkage and stress, separately cured layers not exceeding 2 mm should be applied [3]. However, restoring cavities, especially deep ones, with multiple increments of resin composite is time-consuming and implies the risk of incorporating air bubbles or contaminants between the increments [4].

To refute the paradigm of incremental layering techniques, the chemical and physical parameters of composite materials had to be re-thought [5]. Lately, a new category of resin composites has been introduced: bulk-fill resin composites

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including low-viscosity (flowable) and high-viscosity (sculptable) material types. In order to obtain good clinical outcomes, several conditions have to be met: thick layers should be optimally cured, while polymerization shrinkage as well as stress should be maintained low with no decrease in marginal quality. One approach to improve the depth of cure is to increase the material's translucency [6]. Optical properties of resin composite restoratives are of obvious importance in a procedure reliant on photoactivation, since they may affect light transmission and therefore monomer conversion upon which mechanical properties and ultimate clinical performance are dependent [7]. To optimize material properties, manufacturers incorporated new advanced composite-filler technologies, pre-polymer shrinkage stress relievers, polymerization modulators, and highly light-reactive photoinitiator systems [5, 8]. Most research regarding bulk-fill resin composites recently focused on flowable materials, and the revealed data are very promising in sense of lower polymerization shrinkage and stress compared with conventional resin composites [9, 10]. Moreover, satisfactory micro-tensile bond strength [11], depth of cure [12], degree of conversion (DC), and flexural strength have been reported for flowable bulk-fill materials [8]. However, flowable bulk-fill resin composites require the placement of a final capping layer made of a regular composite material on top of the up to 4-mm-thick composite base, as a result of their low surface hardness and modulus of elasticity [13]. High-viscosity bulk-fill resin composites, in contrast, are indicated for use without veneering, and can thus be applied as true single-step bulk-fill materials. Nevertheless, to date, very few studies concentrated on high-viscosity bulk-fill resin composites and examined their characteristics [6, 13–15], and only one study [16] used Fourier transform infrared spectroscopy (FTIR) to determine the DC of two representatives of non-flowable bulk-fill materials. To the knowledge of the authors, until now, there are no studies dealing with a systematic and thorough investigation on the influence of irradiation time and composite thickness on the DC of currently available high-viscosity bulk-fill resin composites.

The DC has a major impact on the ultimate success of a resin composite restoration [17, 18]. Adequate polymerization results in enhanced physical properties [19] and decreased cytotoxicity of dimethacrylate-based composites [20]. Different factors such as filler particle size and loading, polymerization initiator concentration [21, 22], monomer type and amount, the shade and translucency of the material [23], intensity and wavelength of the light source, as well as irradiation time [24] can influence the DC of dental composite materials. DC is frequently measured to evaluate photopolymerization efficiency by spectroscopic techniques that infer the quantity of remaining double bonds, either mid-infrared Fourier transform (FT) spectroscopy [25], Raman spectroscopy [26] or near-infrared FT spectroscopy (FT NIR) [27]. Microhardness is one of the indirect methods to determine depth of cure [28, 29]. The depth at which a resin composite achieves 80 % of its surface hardness [30, 31] or, more conservative, 80 % of its maximum hardness [14] is generally regarded as the maximum depth at which a resin composite should be used.

The aim of this study was to determine the influence of different irradiation times (10, 20, and 30 s) and composite thicknesses (0.1, 2, 4, 5, and 6 mm) on the DC and microhardness of four high-viscosity bulk-fill resin composites and one conventional nano-hybrid composite material. The null hypotheses tested were as follows: (1) There would be no significant difference within each bulk-fill resin composite and the conventional nano-hybrid composite material in the DC and microhardness achieved at different depths. (2) There would be no significant difference within each bulk-fill resin composite and the conventional nano-hybrid composite material in the DC and microhardness achieved with different irradiation times.

Materials and methods

Table 1 represents the materials used in this study, lot numbers, and manufacturers' information. Four high-viscosity bulk-fill resin composites [Tetric EvoCeram Bulk Fill—TECBF (Ivoclar Vivadent, Schaan, Liechtenstein), x-tra fil—XF (VOCO, Cuxhaven, Germany), QuixFil—QF (Dentsply DeTrey, Konstanz, Germany), SonicFill—SF (Kerr, Orange, CA, USA)], and one conventional nano-hybrid composite material [Tetric EvoCeram—TEC (Ivoclar Vivadent)] were irradiated for 10, 20, or 30 s with a polywave LED curing unit (Bluephase G2, Ivoclar Vivadent) in high-intensity mode. The output light intensity of the curing unit (1,170 mW/cm^2) was measured using a calibrated FieldMaxII-TO power meter in combination with a PM2 thermopile sensor (Coherent, Santa Clara, CA, USA), and verified periodically during the experiments. The study was conducted in two parts: the first part focused on the DC measurements, whereas the second part aimed to evaluate microhardness of the test materials. DC and microhardness were recorded after 24-h dark storage (37 °C) at five measuring depths: 0.1, 2, 4, 5, and 6 mm.

Degree of conversion

A thin wafer of composite paste was compressed between two Mylar strips under 10^7 Pa (Carver press, Specac Ltd., Orpington, Kent, UK). For near-surface measurements (0.1 mm), composite specimens (diameter, 10 mm; thickness, 0.1 mm) were irradiated by pressing the light guide tip of the curing unit against the upper Mylar strip. For measurements at a particular depth, uncured overlays (diameter, 10 mm) of the respective composite material were placed in appropriate

Table 1 Manufacturers' information about the resin composite materials used in the study

Composite material (code)	Manufacturer	Shade/LOT	Resin composition	Filler amount (wt%/vol%), composition and size	Manufacturers' recommended composite layer thickness	Manufacturers' recommended curing time
Tetric EvoCeram (TEC)	Ivoclar Vivadent, Schaan, Liechtenstein	A2/P80726	Bis-GMA, Bis-EMA, UDMA	76/55 Barium glass, YbF_3, mixed oxide, PPF (0.04–3 μm)	2 mm	≥1,000 mW/cm^2/10 s; ≥500 mW/cm^2/20 s
Tetric EvoCeram Bulk Fill (TECBF)	Ivoclar Vivadent, Schaan, Liechtenstein	IVA/R04686	Bis-GMA, Bis-EMA, UDMA	81/61 Barium glass, YbF_3, mixed oxide, PPF (0.04–3 μm)	4 mm	≥1,000 mW/cm^2/10 s; ≥500 mW/cm^2/20 s
x-tra fil (XF)	VOCO, Cuxhaven, Germany	Universal/1205222	Bis-GMA, UDMA, TEGDMA	86/70 Barium boron aluminum silicate glass (0.05–10 μm)	4 mm	≥800 mW/cm^2/10 s; 500–800 mW/cm^2/20 s
QuixFil (QF)	Dentsply DeTrey, Konstanz, Germany	Universal/1202000268	Bis-EMA, UDMA, TEGDMA, di- and trimethacrylate resins, carboxylic acid modified dimethacrylate resin	86/66 Strontium aluminum sodium fluoride phosphate silicate glass (1–10 μm)	4 mm	≥800 mW/cm^2/10 s; 500–800 mW/cm^2/20 s
SonicFill (SF)	Kerr, Orange, CA, USA	A2/4427300	Bis-GMA, Bis-EMA, TEGDMA	84/66 NP	5 mm	>550 mW/cm^2/20 s

Bis-GMA bisphenol-A-glycidyldimethacrylate, *Bis-EMA* ethoxylated bisphenol-A-dimethacrylate, *PPF* prepolymerized fillers, *TEGDMA* triethylene glycol dimethacrylate, *UDMA* urethane dimethacrylate, *YbF_3* ytterbium trifluoride, *NP* filler composition and size not provided

thickness (2, 4, 5, or 6 mm) above the upper Mylar strip, and irradiation was performed in direct contact of the light guide tip to a Mylar strip covering the top of the overlay. Additionally, unpolymerized specimens were used as a reference to determine the proportion of aliphatic and aromatic bonds in cured and uncured material. Soft uncured composite specimens cannot be placed in the sample holder, so they had to be homogenized with spectroscopically pure potassium bromide (Merck, Darmstadt, Germany) in an agate mortar and then pressed into thin pellets in order to be able to perform measurements in transmission mode.

DC (n=5 per group) was measured after 24-h storage in the dark at 37 °C by Fourier transform infrared spectroscopy (FTIR; Model 2000, Perkin Elmer, Beaconsfield, Bucks, UK) [32]. Recording and processing of absorption spectra of the composite specimens were carried out with Spectrum v5.3.1 software (Perkin Elmer). Spectra of unpolymerized and polymerized composite specimens were recorded in transmission mode at room temperature (22 °C), corrected by subtracting the background, and then converted into the absorbance mode. A total of 20 scans per specimen were measured at a resolution of 4 cm^{-1}. The peak ratios were calculated according to Rueggeberg's baseline method [33]. DC was calculated from the equivalent aliphatic (1638 cm^{-1})/aromatic (1610 cm^{-1}) molar ratios of cured (C) and uncured (U) composite specimens according to the following equation:

$$\mathrm{DC}\,(\%) = (1 - \mathrm{C/U}) \times 100$$

Knoop microhardness

For microhardness measurements, a stainless steel mold with a semicircular notch (diameter, 4 mm; length, 8 mm) was used. The semicircular notch was filled in bulk with one of the five resin composites (n=8 per group) and covered with a Mylar strip. The composite material was made flush with the mold using a glass plate, and, after removing the glass plate, the mold was covered with a stainless steel shell [4]. A second Mylar strip was placed on the semicircular opening, and the resin composite was irradiated through the semicircular opening (top surface) keeping the light tip centered and in contact with the second Mylar strip. After irradiation, the shell and both Mylar strips were removed, and the molds containing the resin composite specimens were stored for 24 h in the dark at 37 °C. Knoop microhardness (KHN) was determined on the resin composite specimens at five distances from the light-exposed surface (0.1, 2, 4, 5, and 6 mm) using a digital microhardness tester (model no. 1600-6106, Buehler, Lake Bluff, IL, USA). A load of 10 g was applied, with a dwell time of 20 s. For each specimen, three indentations were performed at each depth (near the middle line) and averaged.

Statistical analysis

ANOVA multivariate analysis and partial eta square statistics were used to investigate the influence of the parameters "composite material", "measuring depth", and "irradiation time" on DC. For each composite material separately, DC and KHN values within each measuring depth and each irradiation time, respectively, were compared using one-way ANOVA followed by Bonferroni's post-hoc test. All analyses were conducted at a pre-set global significance level of $\alpha=0.05$ (SPSS Version 17, SPSS, Chicago, IL, USA).

Results

ANOVA multivariate test revealed that the three factors "composite material" ($p<0.001$), "measuring depth" ($p<0.001$), and "irradiation time" ($p<0.001$) significantly affected DC. The composite material was the parameter with the strongest influence on DC ($\eta^2=0.992$), followed by measuring depth ($\eta^2=0.978$), and irradiation time ($\eta^2=0.965$). Significant interaction effects were observed between the factors "irradiation time" and "composite material" ($p<0.001$), and between "measuring depth" and "composite material" ($p<0.001$).

Table 2 represents the DC obtained with 10-, 20- and 30-s irradiation time at depths of 0.1, 2, 4, 5, and 6 mm. With increasing bulk thickness, DC significantly decreased for TEC with all irradiation times. TECBF and SF showed a significant decrease in DC at 4-mm depth in case of 10-s irradiation, but not with 30-s irradiation. XF and QF demonstrated no significant decrease in DC at depths up to 6 mm when irradiation was performed for at least 20 s. All materials tested achieved more than 80 % of their maximum DC value at depths up to at least 4 mm, irrespective of irradiation time (Table 3). In addition, XF and QF satisfied the same criterion up to 6-mm depth with all irradiation times.

KHN values of all experimental groups are presented in Table 4. KHN of TEC significantly decreased with increasing bulk thickness. TECBF and SF showed a significant decrease in KHN at 4-mm depth in case of both 20- and 30-s irradiation, and at 2 mm in case of 10-s irradiation. With 30-s irradiation time, QF showed no significant KHN decrease for depths up to 6 mm, while this was true for XF for depths up to 5 mm. KHN significantly decreased at 4 mm when XF was irradiated for 20 s or less, and when QF was irradiated for 10 s. At 4-mm depth, only XF and QF irradiated for 30 s achieved at least 80 % of their maximum KHN value (Table 5). However, at 2-mm depth, all bulk-fill resin composites except TECBF attained significantly higher hardness values than at the superficial layer (0.1 mm) in case of 30 s of irradiation (Table 4).

Discussion

This study evaluated the influence of different irradiation times and composite thicknesses on the DC and microhardness of

Table 2 Mean degree of conversion and standard deviations (SD) of the tested composite materials at five measuring depths at 24 h post-irradiation ($n=5$)

Composite material	Irradiation time	0.1 mm		2 mm		4 mm		5 mm		6 mm	
		Mean (%)	SD	Mean (%)	SD	Mean (%)	SD	Mean (%)	SD	Mean (%)	SD
TEC	10 s	71.0 Aa	0.7	65.9 Ba	1.2	59.8 Ca	0.9	52.5 Da	2.2	41.9 Da	4.8
	20 s	71.2 Aa	0.9	70.4 Ab	1.0	65.1 Bb	1.0	58.9 Cb	1.6	48.4 Cab	3.7
	30 s	70.6 Aa	0.7	70.1 Ab	0.6	66.9 Bb	0.6	63.8 Cc	0.9	52.9 Db	0.6
TECBF	10 s	69.9 Aa	0.3	68.7 Aa	1.9	64.1 Ba	0.6	60.6 Ca	1.0	57.4 Ca	1.6
	20 s	71.3 Aab	0.6	71.3 Aa	0.7	68.3 Bb	1.0	65.2 BCb	0.9	63.3 Cb	1.1
	30 s	71.9 Ab	0.8	72.1 Aa	0.9	69.4 ABb	1.1	67.7 Bc	0.6	65.5 Cb	0.6
XF	10 s	70.2 Aa	0.2	71.6 Ba	0.7	71.6 Ba	0.7	67.7 Ca	0.9	63.7 Da	1.3
	20 s	72.1 ABb	0.7	74.0 ABb	0.8	73.9 Ab	0.9	72.6 ABb	1.1	70.8 Bb	0.7
	30 s	71.5 Ab	0.6	74.2 Bb	0.3	74.6 Bb	0.3	74.0 Bc	0.6	72.3 ABb	1.2
QF	10 s	71.1 ABa	1.6	73.0 Aa	1.0	71.9 ABa	0.8	69.5 Ba	1.5	69.2 Ba	1.0
	20 s	74.1 Aa	0.3	74.7 Aa	0.7	74.7 Ab	1.1	72.6 Aab	0.9	73.9 Ab	1.0
	30 s	74.0 Aa	1.8	74.6 Aa	1.1	75.6 Ab	0.7	74.2 Ab	1.2	74.5 Ab	1.2
SF	10 s	76.0 Aab	0.4	76.2 Aa	1.4	67.5 Ba	0.9	53.5 Ca	2.1	32.9 Da	6.7
	20 s	74.9 Aa	0.9	78.9 Ba	0.9	75.5 Ab	1.3	67.7 Cb	1.9	56.4 Db	1.9
	30 s	77.4 Ab	0.7	81.1 Bb	1.3	77.0 Ab	0.9	71.6 Cb	1.2	64.1 Dc	3.3

TEC Tetric EvoCeram, *TECBF* Tetric EvoCeram Bulk Fill, *XF* x-tra fil, *QF* QuixFil, *SF* SonicFill. Different uppercase letters in each row, and different lowercase letters in each column, indicate significant differences within the same material ($p<0.05$; Bonferroni's post-hoc test)

Table 3 Degree of conversion expressed as percentages from the maximum value for each material

Composite material	Irradiation time	0.1 mm (%)	2 mm (%)	4 mm (%)	5 mm (%)	6 mm (%)
TEC	10 s	99.7	92.5	84.0	73.7	58.8
	20 s	100.0	98.9	91.4	82.7	68.0
	30 s	99.2	98.4	94.0	89.6	74.3
TECBF	10 s	96.9	95.3	88.9	84.0	79.6
	20 s	98.9	98.9	94.7	90.4	87.8
	30 s	99.7	100.0	96.2	93.9	90.8
XF	10 s	94.1	96.0	96.0	90.7	85.4
	20 s	96.6	99.2	99.1	97.3	94.9
	30 s	95.8	99.5	100.0	99.2	96.9
QF	10 s	94.0	96.6	95.1	91.9	91.5
	20 s	98.0	98.8	98.8	96.0	97.7
	30 s	97.9	98.7	100.0	98.1	98.5
SF	10 s	93.7	93.9	83.2	66.0	40.6
	20 s	92.3	97.3	93.1	83.5	69.5
	30 s	95.4	100.0	94.9	88.3	79.0

TEC Tetric EvoCeram, *TECBF* Tetric EvoCeram Bulk Fill, *XF* x-tra fil, *QF* QuixFil, *SF* SonicFill

four high-viscosity bulk-fill resin composites and one conventional nano-hybrid composite material. For this purpose, FTIR analysis and KHN evaluation were used. Bulk-fill materials are an emerging class of resin-based dental composites, which is claimed to enable the restoration build-up in thick layers up to 4 or even 5 mm. Depth of cure of light-curing resin composites is a function of filler size and filler composition, shade and translucency of the material, intensity of the light source, duration of irradiation exposure, as well as monomer composition and polymerization initiator concentration [34–36]. Our results revealed a wide variety of different influences on final DC and KHN of the tested bulk-fill resin composites. The composite material was the parameter with the strongest influence on DC, followed by measuring depth and irradiation time. Significant interaction effects between the irradiation time and the tested material as well as between the measuring depth and the tested material were found. This indicates that the DC for different irradiation times and at different measuring depths differed between the tested materials.

Table 4 Mean Knoop hardness and standard deviations (SD) of the tested composite materials at five measuring depths at 24 h post-irradiation (n=8)

Composite material	Irradiation time	0.1 mm		2 mm		4 mm		5 mm		6 mm	
		Mean (KHN)	SD	Mean (KHN)	SD	Mean (KHN)	SD	Mean (KHN)	SD	Mean (KHN)	SD
TEC	10 s	15.1 Aa	0.6	6.8 Ba	0.5	0.6 Ca	0.1	–	–	–	–
	20 s	18.5 Ab	2.0	11.7 Bb	1.2	2.6 Cb	0.3	–	–	–	–
	30 s	16.9 Aab	1.2	14.5 Bc	0.9	4.4 Cc	0.3	1.4 Da	0.2	–	–
TECBF	10 s	16.5 Aa	1.2	12.0 Ba	0.7	3.8 Ca	0.3	1.5 Da	0.2	–	–
	20 s	19.9 Ab	1.8	20.1 Ab	1.2	9.2 Bb	0.8	4.5 Cb	0.7	2.0 Da	0.4
	30 s	20.5 Ab	2.0	22.8 Ac	1.4	13.0 Bc	0.7	7.6 Cc	0.5	4.1 Db	0.2
XF	10 s	22.6 Aa	1.4	20.4 Aa	2.0	11.0 Ba	1.2	6.1 Ca	1.1	3.2 Da	0.7
	20 s	28.3 Ab	2.2	32.6 Ab	2.2	20.2 Bb	0.8	14.2 Cb	2.1	8.7 Db	1.4
	30 s	24.6 Ac	1.4	36.7 Bc	1.7	30.7 Cc	2.0	21.7 Ac	1.6	14.6 Dc	1.5
QF	10 s	21.6 Aa	1.0	21.3 Aa	0.7	12.6 Ba	1.0	9.2 Ca	0.8	5.1 Da	0.5
	20 s	26.2 Ab	1.5	31.7 Bb	1.4	25.0 Ab	1.3	17.5 Cb	2.0	13.4 Db	1.8
	30 s	22.4 Aa	0.9	36.5 Bc	0.9	31.0 Cc	2.5	26.9 ACc	2.7	23.6 Ac	2.0
SF	10 s	21.7 Aa	1.2	16.7 Ba	1.8	–	–	–	–	–	–
	20 s	26.1 Ab	2.4	29.5 Bb	1.5	9.6 Ca	0.8	–	–	–	–
	30 s	28.9 Ac	2.5	36.0 Bc	3.0	15.3 Cb	2.7	–	–	–	–

TEC Tetric EvoCeram, *TECBF* Tetric EvoCeram Bulk Fill, *XF* x-tra fil, *QF* QuixFil, *SF* SonicFill. Different uppercase letters in each row, and different lowercase letters in each column, indicate significant differences within the same material ($p<0.05$; Bonferroni's post-hoc test)

Table 5 Knoop hardness expressed as percentages from the maximum value for each material

Composite material	Irradiation time	0.1 mm (%)	2 mm (%)	4 mm (%)	5 mm (%)	6 mm (%)
TEC	10 s	81.6	37.0	3.1	–	–
	20 s	100.0	63.4	14.0	–	–
	30 s	91.6	78.3	24.1	7.8	–
TECBF	10 s	72.2	52.8	16.7	6.4	–
	20 s	87.4	88.1	40.2	19.7	8.9
	30 s	90.0	100.0	57.2	33.5	17.8
XF	10 s	61.6	55.6	29.9	16.7	8.7
	20 s	77.1	88.9	55.1	38.7	23.7
	30 s	67.0	100.0	83.6	59.2	39.7
QF	10 s	59.0	58.4	34.4	25.2	13.9
	20 s	71.8	86.9	68.6	47.8	36.6
	30 s	61.4	100.0	84.9	73.7	64.6
SF	10 s	60.3	46.5	–	–	–
	20 s	72.5	81.9	26.7	–	–
	30 s	80.4	100.0	42.6	–	–

TEC Tetric EvoCeram, *TECBF* Tetric EvoCeram Bulk Fill, *XF* x-tra fil, *QF* QuixFil, *SF* SonicFill

The setting process has a major impact on the final mechanical, physical, and biological properties of dimethacrylate-based dental composites [37]. Resin polymerization depends mainly on intrinsic factors such as the chemical structure of the monomer and photoinitiator concentration, and extrinsic factors such as the polymerization conditions [1]. While the number of photons that reach the cavity floor is significantly lower than the number of photons that reach the surface, there are several approaches aiming to increase the curing depth of resin composites, e.g., to improve the absorption spectrum and the initiator's reactivity, to optimize the LED light source, and to increase the translucency of the materials [38, 39].

Concerning the first approach, the most commonly used photoinitiator is a combination of camphorquinone (CQ) and generally different types of tertiary amines [40]. Numerous photoinitiators have been considered as alternative curing systems such as phenylpropanedione (PPD), mono- or bis-acylphosphine oxides (MAPO and BAPO), benzoyl germanium, or else benzil [41–44]. Each converted CQ molecule only generates one free radical that will actually initiate polymerization. Other photoinitiators are able to generate several active radicals per molecule, e.g., two for MAPO and four for BAPO [44, 45]. This explains the lower polymerization quantum yield of CQ, which is the amount of monomer polymerized per absorbed photon [44]. New photoinitiators like dibenzoyl germanium derivates are far more light-reactive than CQ [46]. Such a germanium-based initiator (Ivocerin) is incorporated in TECBF as an additional photoinitiator besides CQ/amine initiator systems, in order to enable the material to polymerize more rapidly and with greater depth of cure. In this study, however, QF revealed the highest DC and KHN at deep layers (5 and 6 mm), which is surprising since, according to the information given by the manufacturer, it only contains CQ as photoinitiator. Though some photoinitiator systems have advantages over the classical CQ system, this should be considered in relation to some intrinsic (co-monomer composition and ratio, filler content and size) and extrinsic factors (such as light spectrum, irradiance, and irradiation time). This is closely connected with the second approach to increase the depth of cure, which deals with light source. "Third-generation" LED curing units [38] have the ability to generate multiple wavelengths from a single LED light in order to attain necessary peaks and, on the other hand, to possess sufficient intensity and adequate shape and size of the light probe. In this study, a polywave light source with high light intensity (1,170 mW/cm^2) was used. However, a great impact of irradiation time on DC and hardness was observed, especially in deep composite layers, thus confirming previous reports [47–49]. The third approach to increase depth of cure is to increase the translucency of resin composites with the aim to ensure that more photons penetrate into deeper areas of the material, where they will activate initiator molecules [38]. It seems that reducing filler content together with increasing filler size plays a crucial role in achieving higher translucency of bulk-fill resin composites [6]. The amount of light transmitted through a composite material depends on the amount of scattered and absorbed light. Light scattering is increased in materials with a large filler-matrix interface area, due to differences in the refractive indices between filler particles and resin matrix [6, 8]. On the other hand, similar refractive indices of the components of resin composites, as demonstrated for Bis-GMA and silica fillers, have been shown to improve translucency in experimental materials, and a linear correlation between the percentage of Bis-GMA in the organic matrix and light transmittance has been established [50]. The following data on the translucency of the test materials were available from the manufacturers: TECBF 15 %, QF 17 %, XF 23 %, and conventional TEC around 10 %. The results yielded in this study revealed a higher DC for the more translucent materials QF and XF compared to TECBF at depths of 2 mm and beyond. In such a way the impact of material translucency on curing depth is highlighted. QF and XF contain the largest filler particles among the resin composites under investigation with up to 10-μm filler size (Table 1), which lowers the specific surface between fillers and organic matrix, thus reducing light scattering and allowing more photons to penetrate the material. Generally, subsurface DC values of all tested bulk-fill materials were higher compared to the conventional nano-hybrid resin composite. Among the tested materials, SF showed high DC values up to 4 mm (up to 77.0 %), but also the largest discrepancy from the manufacturer's recommendation was observed for depth of cure of SF based on KHN data. This finding might be explained by the fact that SF, unlike other bulk-fill resin composites, is not more translucent for blue light than conventional composite materials, due to its high filler content (84 wt%, 66 vol%) and irregularly shaped particles, which increase light scattering and thus decrease light transmittance [6]. Our results are supported by Garcia et al. [51] and Garoushi et al. [52], but in contrast to another study [14].

The DC is known to evolve up to about 24 h after irradiation [53]. Moreover, the temperature during polymerization can significantly affect polymerization efficiency, and a rise from room temperature (22 °C) to mouth temperature (35 °C) has been shown to result in increased DC due to improved monomer mobility [54]. Taking these parameters that influence the final DC, in the present study, all measurements were conducted after 24-h dark storage at 37 °C. Dental polymers based on Bis-EMA and lower viscosity (higher molecular mobility) urethane derivates usually exhibit higher DC than the typical Bis-GMA/TEGDMA resins [55, 56]. Consequently, the high DC of QF through depth might not only be attributed to the high translucency of the material, but also to its favorable resin composition containing Bis-EMA, UDMA, and TEGDMA, but no Bis-GMA (Table 1).

In addition to direct spectroscopic techniques, DC has also been indirectly evaluated by microhardness measurements [57], and a good linear correlation has generally been observed between DC and microhardness [28, 58, 59]. In the present study, however, whereas it was possible to measure DC of the tested materials at all depths, this was not the case for KHN, due to softness in the following conditions: TEC at 5 mm (10- and 20-s irradiation time) and at 6 mm (all irradiation times), TECBF at 6 mm (10-s irradiation time), and SF at 4 mm (10-s irradiation time), and at 5 and 6 mm (all irradiation times). The discrepancies between the DC and KHN results might be basically related to the fact that the composite specimens for the FTIR measurements differed from those for the hardness tests in their dimensions, geometry, and surface conditions.

KHN values recorded in the present study were lower compared to those measured in other studies that analyzed microhardness of high-viscosity bulk-fill resin composites [6, 13]. The lower hardness values might be due to the fact that, in order to avoid any heat production, the composite specimens were not ground or polished prior to hardness testing, so that measurements were performed on the specimens' resin-rich outer layer [54]. Furthermore, a relatively low indenter load of 10 g was used in this study, which has been shown to result in lower KHN values compared to those recorded after higher indenter load application [60]. Finally, it has been recently established that the distribution of KHN is non-uniform within molds and that KHN is substantially lower at or near the mold walls than at the center [61]. In the present study, a hemicylindrical mold was used, and hardness measurements were performed along the surface that had been in contact with the stainless steel shell (and, thus, with the former mold wall). It should be pointed out, that the intention of this investigation was not to compare absolute hardness values recorded in our study with those of other studies, but to use KHN to study depth of cure.

Previous studies used the bottom-to-top Knoop hardness ratio to estimate depth of cure of composite materials, and if the value exceeded 80 %, the specimens were considered to be adequately cured [31, 62]. It should be noted, however, that other factors than DC also affect microhardness, notably the degree of crosslinking [63]. Thus, higher DC does not necessarily result in higher mechanical properties [64, 65]. In any case, KHN measurements do not provide any quantitative information on the actual change in reactive groups. In the present investigation, both DC and KHN data was used for assessment of depth of cure. Calculations were based on the 80 % level of the maximum DC and KHN value for each material, thus providing a more conservative estimate of curing depth than if upper surface DC/KHN was used as reference value, which does not take into account that maximum conversion/hardness is typically not attained directly at the surface of the specimens, but at a level slightly below the surface [8, 66–68]. Current data indicate that all tested bulk-fill resin composites achieved at least 80 % of their maximum DC value at the manufacturers' claimed maximum incremental thickness of 4 mm (SF, 5 mm) or beyond with irradiation times stated by the manufacturers (10 s for TECBF, XF, and QF; 20 s for SF). Even though all resin composites met the 80 % DC threshold at 4-mm incremental thickness with an irradiation time as short as 10 s, the attained DC of TEC, TECBF, and SF was nevertheless significantly lower at 4-mm depth than at the upper surface, and all materials irradiated for 10 s reached significantly lower monomer conversion at 4-mm depth than when irradiation was performed for at least 20 s. Furthermore, at 4-mm depth, only two of the four tested bulk-fill materials (QF and XF) achieved at least 80 % of their maximum KHN value, under the condition that irradiation time was extended to 30 s. In accordance with previous reports [67, 69], our results thus revealed higher depth of cure of the resin composites under investigation when calculations were based on DC data than when based on microhardness. It needs to be emphasized, however, that the two methods used for assessment of depth of cure in the present study are means to gain insight into two different aspects of the same material. While depth of cure based on conversion refers to the amount of unreacted monomer species and thus implies relative biocompatibility, depth of cure based on hardness suggests mechanical stability of a composite material through depth. Both aspects should be taken into account when giving clinical recommendations regarding composite layer thicknesses.

Conclusions

Increasing the irradiation time increases the DC and KHN in deeper composite layers. At 4-mm depth, the significantly lowest DC and KHN were observed when irradiation was performed for 10 s, irrespective of the bulk-fill material, thus conflicting with the irradiation time of 10 s recommended by some of the manufacturers. An irradiation time of 20–30 s, dependent upon the specific material, with a high-intensity light-curing unit might ensure adequate double bond conversion of the tested bulk-fill resin composites at depths up to at least 4 mm. However, not all bulk-fill materials attained the 80 % KHN threshold at 4-mm depth with up to 30 s of irradiation, even though the 80 % DC threshold was met. Thus, taking DC and KHN results together, the placement of 4-mm composite increments cannot be generally recommended for all high-viscosity bulk-fill materials under investigation, at least at irradiation times ≤30 s. The tested null hypotheses were rejected.

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Conflict of interest The authors declare that they have no conflict of interest.

References

1. Leprince JG, Palin WM, Hadis MA, Devaux J, Leloup G (2013) Progress in dimethacrylate-based dental composite technology and curing efficiency. Dent Mater 29:139–156
2. Roggendorf MJ, Kramer N, Appelt A, Naumann M, Frankenberger R (2011) Marginal quality of flowable 4-mm base vs. conventionally layered resin composite. J Dent 39:643–647
3. Ferracane JL (2011) Resin composite—state of the art. Dent Mater 27:29–38
4. Flury S, Hayoz S, Peutzfeldt A, Husler J, Lussi A (2012) Depth of cure of resin composites: is the ISO 4049 method suitable for bulk fill materials? Dent Mater 28:521–528
5. Manhart J, Hickel R (2014) Bulk-fill-composites. Modern application technique of direct composites for posterior teeth. Swiss Dent J 124:19–37
6. Bucuta S, Ilie N (2014) Light transmittance and micro-mechanical properties of bulk fill vs. conventional resin based composites. Clin Oral Investig. doi: 10.1007/s00784-013-1177-y
7. Howard B, Wilson ND, Newman SM, Pfeifer CS, Stansbury JW (2010) Relationships between conversion, temperature and optical properties during composite photopolymerization. Acta Biomater 6: 2053–2059
8. Czasch P, Ilie N (2013) In vitro comparison of mechanical properties and degree of cure of bulk fill composites. Clin Oral Investig 17:227–235
9. Tauböck TT, Feilzer AJ, Buchalla W, Kleverlaan CJ, Krejci I, Attin T (2014) Effect of modulated photo-activation on polymerization shrinkage behavior of dental restorative resin composites. Eur J Oral Sci 122:293–302
10. Ilie N, Hickel R (2011) Investigations on a methacrylate-based flowable composite based on the SDR^{TM} technology. Dent Mater 27:348–355
11. Van Ende A, De Munck J, Van Landuyt KL, Poitevin A, Peumans M, Van Meerbeek B (2013) Bulk-filling of high C-factor posterior cavities: effect on adhesion to cavity-bottom dentin. Dent Mater 29:269–277
12. Finan L, Palin WM, Moskwa N, McGinley EL, Fleming GJ (2013) The influence of irradiation potential on the degree of conversion and mechanical properties of two bulk-fill flowable RBC base materials. Dent Mater 29:906–912
13. Ilie N, Bucuta S, Draenert M (2013) Bulk-fill resin-based composites: an in vitro assessment of their mechanical performance. Oper Dent 38:618–625
14. Alrahlah A, Silikas N, Watts DC (2014) Post-cure depth of cure of bulk fill dental resin-composites. Dent Mater 30:149–154
15. Furness A, Tadros MY, Looney SW, Rueggeberg FA (2014) Effect of bulk/incremental fill on internal gap formation of bulk-fill composites. J Dent 42:439–449
16. Goracci C, Cadenaro M, Fontanive L, Giangrosso G, Juloski J, Vichi A, Ferrari M (2014) Polymerization efficiency and flexural strength of low-stress restorative composites. Dent Mater 30:688–694
17. Yoon TH, Lee YK, Lim BS, Kim CW (2002) Degree of polymerization of resin composites by different light sources. J Oral Rehabil 29:1165–1173
18. Chung KH (1990) The relationship between composition and properties of posterior resin composites. J Dent Res 69:852–856
19. Poskus LT, Placido E, Cardoso PE (2004) Influence of placement techniques on Vickers and Knoop hardness of class II composite resin restorations. Dent Mater 20:726–732
20. Sigusch BW, Pflaum T, Volpel A, Gretsch K, Hoy S, Watts DC, Jandt KD (2012) Resin-composite cytotoxicity varies with shade and irradiance. Dent Mater 28:312–319
21. Miletic V, Santini A (2012) Optimizing the concentration of 2,4,6-trimethylbenzoyldiphenylphosphine oxide initiator in composite resins in relation to monomer conversion. Dent Mater J 31:717–723
22. Turssi CP, Ferracane JL, Vogel K (2005) Filler features and their effects on wear and degree of conversion of particulate dental resin composites. Biomaterials 26:4932–4937
23. Tarle Z, Meniga A, Ristic M, Sutalo J, Pichler G, Davidson CL (1998) The effect of the photopolymerization method on the quality of composite resin samples. J Oral Rehabil 25:436–442

24. Uctasli S, Tezvergil A, Lassila LV, Vallittu PK (2005) The degree of conversion of fiber-reinforced composites polymerized using different light-curing sources. Dent Mater 21:469–475
25. Ferracane JL, Greener EH (1984) Fourier transform infrared analysis of degree of polymerization in unfilled resins—methods comparison. J Dent Res 63:1093–1095
26. Pianelli C, Devaux J, Bebelman S, Leloup G (1999) The micro-Raman spectroscopy, a useful tool to determine the degree of conversion of light-activated composite resins. J Biomed Mater Res 48: 675–681
27. Stansbury JW, Dickens SH (2001) Determination of double bond conversion in dental resins by near infrared spectroscopy. Dent Mater 17:71–79
28. Ferracane JL (1985) Correlation between hardness and degree of conversion during the setting reaction of unfilled dental restorative resins. Dent Mater 1:11–14
29. Asmussen E (1982) Restorative resins: hardness and strength vs. quantity of remaining double bonds. Scand J Dent Res 90: 484–489
30. Cohen ME, Leonard DL, Charlton DG, Roberts HW, Ragain JC (2004) Statistical estimation of resin composite polymerization sufficiency using microhardness. Dent Mater 20:158–166
31. Soh MS, Yap AU, Siow KS (2003) The effectiveness of cure of LED and halogen curing lights at varying cavity depths. Oper Dent 28: 707–715
32. Tarle Z, Meniga A, Ristic M, Sutalo J, Pichler G (1995) Polymerization of composites using pulsed laser. Eur J Oral Sci 103:394–398
33. Rueggeberg FA, Hashinger DT, Fairhurst CW (1990) Calibration of FTIR conversion analysis of contemporary dental resin composites. Dent Mater 6:241–249
34. Tauböck TT, Oberlin H, Buchalla W, Roos M, Attin T (2011) Comparing the effectiveness of self-curing and light curing in polymerization of dual-cured core buildup materials. J Am Dent Assoc 142:950–956
35. Tauböck TT, Buchalla W, Hiltebrand U, Roos M, Krejci I, Attin T (2011) Influence of the interaction of light- and self-polymerization on subsurface hardening of a dual-cured core build-up resin composite. Acta Odontol Scand 69:41–47
36. Polydorou O, Manolakis A, Hellwig E, Hahn P (2008) Evaluation of the curing depth of two translucent composite materials using a halogen and two LED curing units. Clin Oral Investig 12:45–51
37. Cramer NB, Stansbury JW, Bowman CN (2011) Recent advances and developments in composite dental restorative materials. J Dent Res 90:402–416
38. Rueggeberg FA (2011) State-of-the-art: Dental photocuring—a review. Dent Mater 27:39–52
39. Leloup G, Holvoet PE, Bebelman S, Devaux J (2002) Raman scattering determination of the depth of cure of light-activated composites: influence of different clinically relevant parameters. J Oral Rehabil 29:510–515
40. Jakubiak J, Allonas X, Fouassier JP, Sionkowska A, Andrzejewska E, Linden LA (2003) Camphorquinone–amines photoinitiating systems for the initiation of free radical polymerization. Polymer 44:5219–5226
41. Neshchadin D, Rosspeintner A, Griesser M, Lang B, Mosquera-Vazquez S, Vauthey E, Gorelik V, Liska R, Hametner C, Ganster B, Saf R, Moszner N, Gescheidt G (2013) Acylgermanes: photoinitiators and sources for Ge-centered radicals. Insights into their reactivity. J Am Chem Soc 135:17314–17321
42. Leprince JG, Hadis M, Shortall AC, Ferracane JL, Devaux J, Leloup G, Palin WM (2011) Photoinitiator type and applicability of exposure reciprocity law in filled and unfilled photoactive resins. Dent Mater 27:157–164
43. Ogunyinka A, Palin WM, Shortall AC, Marquis PM (2007) Photoinitiation chemistry affects light transmission and degree of conversion of curing experimental dental resin composites. Dent Mater 23:807–813
44. Neumann MG, Schmitt CC, Ferreira GC, Correa IC (2006) The initiating radical yields and the efficiency of polymerization for various dental photoinitiators excited by different light curing units. Dent Mater 22:576–584
45. Decker C (2002) Kinetic study and new applications of UV radiation curing. Macromol Rapid Commun 23:1067–1093
46. Moszner N, Fischer UK, Ganster B, Liska R, Rheinberger V (2008) Benzoyl germanium derivatives as novel visible light photoinitiators for dental materials. Dent Mater 24:901–907
47. Tauböck TT, Bortolotto T, Buchalla W, Attin T, Krejci I (2010) Influence of light-curing protocols on polymerization shrinkage and shrinkage force of a dual-cured core build-up resin composite. Eur J Oral Sci 118:423–429
48. Scotti N, Venturello A, Migliaretti G, Pera F, Pasqualini D, Geobaldo F, Berutti E (2011) New-generation curing units and short irradiation time: the degree of conversion of microhybrid composite resin. Quintessence Int 42:e89–95
49. Yap AU (2000) Effectiveness of polymerization in composite restoratives claiming bulk placement: impact of cavity depth and exposure time. Oper Dent 25:113–120
50. Azzopardi N, Moharamzadeh K, Wood DJ, Martin N, van Noort R (2009) Effect of resin matrix composition on the translucency of experimental dental composite resins. Dent Mater 25:1564–1568
51. Garcia D, Yaman P, Dennison J, Neiva G (2014) Polymerization shrinkage and depth of cure of bulk fill flowable composite resins. Oper Dent 39:441–448
52. Garoushi S, Sailynoja E, Vallittu PK, Lassila L (2013) Physical properties and depth of cure of a new short fiber reinforced composite. Dent Mater 29:835–841
53. Truffier-Boutry D, Demoustier-Champagne S, Devaux J, Biebuyck JJ, Mestdagh M, Larbanois P, Leloup G (2006) A physico-chemical explanation of the post-polymerization shrinkage in dental resins. Dent Mater 22:405–412
54. Price RB, Whalen JM, Price TB, Felix CM, Fahey J (2011) The effect of specimen temperature on the polymerization of a resin-composite. Dent Mater 27:983–989
55. Stansbury JW (2012) Dimethacrylate network formation and polymer property evolution as determined by the selection of monomers and curing conditions. Dent Mater 28:13–22
56. Skrtic D, Antonucci JM (2007) Effect of chemical structure and composition of the resin phase on vinyl conversion of amorphous calcium phosphate-filled composites. Polym Int 56:497–505
57. Manhart J, Chen HY, Hickel R (2001) The suitability of packable resin-based composites for posterior restorations. J Am Dent Assoc 132:639–645
58. Rueggeberg FA, Craig RG (1988) Correlation of parameters used to estimate monomer conversion in a light-cured composite. J Dent Res 67:932–937
59. DeWald JP, Ferracane JL (1987) A comparison of four modes of evaluating depth of cure of light-activated composites. J Dent Res 66: 727–730
60. Uhl A, Michaelis C, Mills RW, Jandt KD (2004) The influence of storage and indenter load on the Knoop hardness of dental composites polymerized with LED and halogen technologies. Dent Mater 20: 21–28
61. Erickson RL, Barkmeier WW (2014) Curing characteristics of a composite. Part 2: the effect of curing configuration on depth and distribution of cure. Dent Mater 30:e134–45
62. Moore BK, Platt JA, Borges G, Chu TM, Katsilieri I (2008) Depth of cure of dental resin composites: ISO 4049 depth and microhardness of types of materials and shades. Oper Dent 33:408–412
63. Soh MS, Yap AU (2004) Influence of curing modes on crosslink density in polymer structures. J Dent 32:321–326

64. Tauböck TT, Zehnder M, Schweizer T, Stark WJ, Attin T, Mohn D (2014) Functionalizing a dentin bonding resin to become bioactive. Dent Mater 30:868–875
65. Marovic D, Panduric V, Tarle Z, Ristic M, Sariri K, Demoli N, Klaric E, Jankovic B, Prskalo K (2013) Degree of conversion and microhardness of dental composite resin materials. J Mol Str 1044:299–302
66. Frauscher KE, Ilie N (2012) Depth of cure and mechanical properties of nano-hybrid resin-based composites with novel and conventional matrix formulation. Clin Oral Investig 16:1425–1434
67. Leprince JG, Leveque P, Nysten B, Gallez B, Devaux J, Leloup G (2012) New insight into the "depth of cure" of dimethacrylate-based dental composites. Dent Mater 28:512–520
68. Onose H, Sano H, Kanto H, Ando S, Hasuike T (1985) Selected curing characteristics of light-activated composite resins. Dent Mater 1:48–54
69. Bouschlicher MR, Rueggeberg FA, Wilson BM (2004) Correlation of bottom-to-top surface microhardness and conversion ratios for a variety of resin composite compositions. Oper Dent 29:698–704