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Real-time Light Transmittance Monitoring for Determining Polymerization Completeness of Conventional and Bulk Fill Dental Composites

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Clinical Relevance

Short curing times of 10-20 seconds may be insufficient for an optimal polymerization, especially under nonideal clinical conditions (eg, variable distance and angulation of the curing unit tip).

SUMMARY

Objectives: To monitor the real-time changes in light transmittance during composite curing and to use transmittance data to determine the curing times required for a complete polymerization.

Methods: Three conventional and three bulk fill composites were cured with two light-emitting diode curing units at layer thicknesses of 2 mm and 4 mm. The real-time light transmittance data were collected by a UV-Vis spectrometer in the wavelength range of 350-550 nm, plotted against time (t) and fitted to an exponential function f(t), whose first derivative $\Delta T(t) = df(t)/dt$ represented the rate of transmittance change. As the changing transmittance reflects structural changes that occur during polymerization, $\Delta T(t) > 0$ was considered to indicate an ongoing polymerization, whereas $\Delta T(t)$ values approaching zero suggested a complete polymerization. This principle was used to determine times required for a complete polymerization ($t_{complete}$) for each material/thickness/curing unit combination.

Results: Light transmittance was significantly influenced by the material type, sample thick-

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ness, and curing unit, amounting to 2.9%-27.0% for the bulk fill and 0.7%-16.7% for the conventional composites. The values of $t_{complete}$ amounted to 15.3-23.3 seconds for the bulk fill composites at 2 mm, 20.2-33.3 seconds for the conventional composites at 2 mm, 26.9-42.1 seconds for the bulk fill composites at 4 mm, and 40.1-59.8 seconds for the conventional composites at 4 mm. Additionally, an exponential relationship was discovered between the light transmittance and $t_{complete}$.

Conclusions: Some of the $t_{complete}$ values considerably exceeded the curing times recommended by the manufacturers.

INTRODUCTION

The need for simplification of the clinical placement of dental composites was addressed by launching the so-called bulk fill composites, which allow layer thicknesses over 2 mm.[1] This class of materials features larger particles or lower filler loads than do conventional composites, both factors acting to enhance the curing light penetration.[2] Together with other advanced compositional modifications that diminish the negative effect of polymerization shrinkage,[3] the bulk fill composites are suitable for placement in layers of 4 mm or thicker.[4,5] Introduction of bulk fill composites has substantially changed the material application technique, allowing most of the clinically encountered cavities to be filled in a single layer. In line with the efforts to further simplify and shorten the clinical placement of composites, some composite manufacturers recommend using high-irradiance curing units for short curing times of 10-20 seconds.[6] Concerns have been raised regarding the polymerization efficiency of such short curing times, indicating that deeper parts of a thick layer might remain undercured.[6,7] Since the monomer conversion of composite restorations is a fundamental property that underlies mechanical features and biocompatibility,[8,9] the clinical procedures should strive to attain the highest conversion values possible. It is thus unreasonable to compromise the monomer conversion at the restoration bottom just for the sake of saving several tens of seconds of chair time. Hence, the manufacturer's recommendations of short curing times should be critically evaluated by different methods. The curing efficiency at depth is usually assessed through measurements of monomer conversion[10] or microhardness,[11] whereas our article presents an alternative approach by using real-time light transmittance monitoring.

Assessing the polymerization progress through light transmittance monitoring is possible because the monomer conversion rise during curing is reflected as the change in light transmittance.[12] The light transmittance changes during polymerization are due to several processes: photoinitiator consumption, temperature increase, polymerization shrinkage, and change of the refractive index of the polymerizing resin.[13] The latter process is considered to make the greatest contribution to the transmittance change during polymerization.[14] Light attenuation in dental composites is chiefly determined by light scattering,[15] which depends on the refractive index mismatch between the resin and filler.[16] While the refractive index of filler remains constant throughout the polymerization, the refractive index of resin rises with monomer conversion.[17] Thus, the light transmittance can be considered a function of monomer conversion, although the exact mathematical relationship is unknown. However, the real-time light transmittance data can be used to assess the completeness of polymerization using a simple and straightforward rationale: the changing transmittance reflects an ongoing polymerization, whereas the plateau of the transmittance curve indicates a "completed" polymerization.[18] This approach neglects the individual contributions of multiple processes that affect the light transmittance change and simply postulates that the nonchanging transmittance equals a complete polymerization. After plotting the real-time light transmittance data as a function of time, the rate of transmittance change can be represented by calculating the first derivative of the transmittance curves. As the graph of the first derivative approaches zero, the polymerization reaction can be considered to near its completion. This principle is presented as a simple and inexpensive means for evaluating the polymerization completeness of dental composites, contrasting the more expensive and equipment-demanding vibrational spectroscopy, which is the standard method for quantifying the extent of polymerization.[19]

The aim of this study was to monitor the light transmittance of conventional and bulk fill composites during light curing and to use the real-time transmittance data to obtain information on polymerization progress. Furthermore, a method is presented for evaluating the curing times required for a complete polymerization. The hypotheses tested were the following: 1) light transmittance differs among composite materials, layer thicknesses, and curing units; 2) the curing time required for a complete polymerization differs among composite

Table 1: *Information About the Composite Materials, as Provided by Their Respective Manufacturers*

Material (Abbreviation)	Shade Lot No. EXP	Composition	Filler Load, wt%/vol%	Manufacturer	Minimum Curing Time (Manufacturer's Recommendation)[a], s
X-tra fil (XF)	U 1441587 2017-04	Bis-GMA, UDMA, TEGDMA, Ba-B-Al-Si glass	86/70	Voco, Cuxhaven, Germany	10 s for >800 mW/cm^2
Filtek Bulk Fil (FBF)	A2 N621319 2017-08	Bis-GMA, Bis-EMA, UDMA, zirconia/silica, ytterbium trifluoride	65/43	3M/ESPE, St Paul, MN, USA	40 s for <1000 mW/cm^2 20 s for >1000 mW/cm^2
Tetric EvoCeram Bulk Fill (TECBF-IVA)	IVA S21840 2017-05	Dimethacrylate, Ba-Al-Si-glass, prepolymer filler (monomer, glass filler and ytterbium fluoride), spherical mixed oxide	80/61 (including 17% prepolymers)	Ivoclar Vivadent, Schaan, Liechtenstein	10 s for >1000 mW/cm^2
Tetric EvoCeram Bulk Fill (TECBF-IVB)	IVB R77065 2016-10				
Tetric EvoCeram (TEC-A2)	A2 T26729 2018-07	UDMA, Bis-GMA, Bis-EMA, ytterbium trifluoride	76/54	Ivoclar Vivadent, Schaan, Liechtenstein	20 s for <1000 mW/cm^2 10 s for >1000 mW/cm^2
Tetric EvoCeram (TEC-A3)	A3 S12959 2018-07				
Gradia Direct Posterior (GDP)	A3 1406252 2017-06	UDMA, dimethacrylate, fluoroaluminosilicate glass	77/65	GC Corp, Tokyo, Japan	20 s for <1200 mW/cm^2 10 s for >1200 mW/cm^2
Grandio (GR)	A3 1428354 2018-01	Ba-Al-Borosilicate glass filler, SiO_2 nanofillers, Bis-GMA, TEGDMA, Bis-EMA	87/71	Voco, Cuxhaven, Germany	20 s for >500 mW/cm^2

Abbreviations: Bis-EMA: ethoxylated bisphenol A dimethacrylate, Bis-GMA: bisphenol A glycidyl methacrylate, TEGDMA: triethylene glycol dimethacrylate, UDMA: urethane dimethacrylate.
[a] *Manufacturers commonly recommend minimal curing time required for complete polymerization of 2- and 4-mm-thick layers for conventional and bulk fill composites, respectively. The recommendation also includes the minimum irradiance of a curing unit for which the listed curing times are advised.*

materials, layer thicknesses, and curing units; 3) the time required for a complete polymerization can be presented as a function of light transmittance; and 4) the curing times recommended by composite manufacturers are sufficient for a complete polymerization of conventional and bulk fill composites when applied in layers of 2 mm and 4 mm, respectively.

METHODS AND MATERIALS

Composite Materials and Light-curing Units

Three conventional and three bulk fill composites were investigated (Table 1). The specifications of light-emitting diode (LED)–based curing units are given in Table 2. The reported irradiance values were checked before and after the study to confirm that there was no decline in the curing unit output. The curing units differed by their irradiances and by radiant spectra; Bluephase Style M8 and Bluephase Style, respectively, featured one and two radiant peaks (Figure 1). Dual radiant peaks are characteristic of the latest generation of LED-curing units and are beneficial for curing composites that contain alternative photoinitiators.[20] The time-dependent radiant profiles recorded for the curing units operating for the longest time available (30 seconds) are shown in Figure 2.

Table 2: *Specifications of the Light-curing Units*

Light-curing Unit	Manufacturer	Emission Maximum, nm[a]	Irradiance: Nominal[b]/True[c], mW/cm^2
Bluephase Style M8	Ivoclar-Vivadent, Schaan, Liechtenstein	441	800/658
Bluephase Style	Ivoclar-Vivadent, Schaan, Liechtenstein	450, 405	1100/938

[a] *Measured with spectrometer HR4000 (Ocean Optics, Dunedin, FL, USA).*
[b] *Provided by the respective manufacturer.*
[c] *Plateau value measured with integrating sphere (IS, Gigahertz Optik GmbH, Puchheim, Germany).*

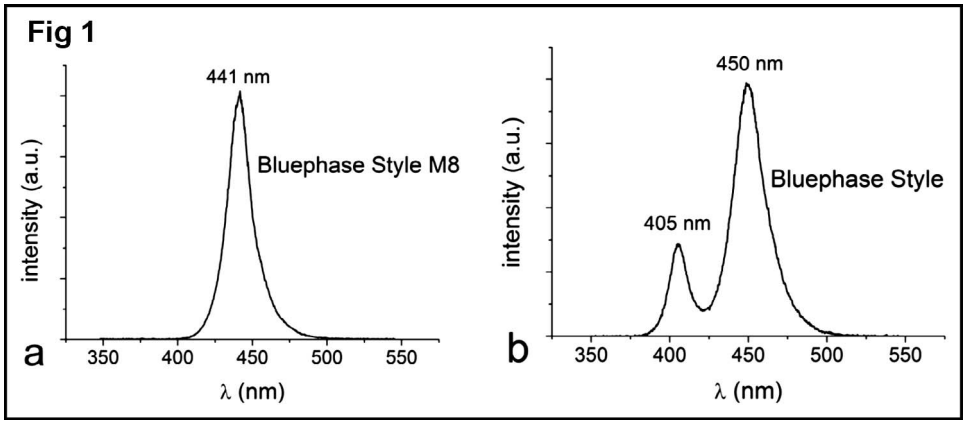

Figure 1. *Emission spectra of the curing units Bluephase Style M8 (a) and Bluephase Style (b).*

Real-time Light Transmittance Measurements

Cylindrical composite samples (diameter=6 mm, height=2 or 4 mm) were prepared in black Teflon molds, and four repeats were performed (n=4) for each combination of material/thickness/curing unit. The small sample size (n=4 per experimental group) was considered sufficient because of the exploratory nature of this study. The experimental setup is described in a previous work.[13] Briefly, the uncured samples were covered from both sides with a polyethylene terephthalate (PET) film and sandwiched between two glass plates. The curing unit tip was centered to the Teflon ring opening immediately below the glass plate, and the light intensity was monitored from the opposite side of the sample. The spectra of transmitted light were recorded by the charge-coupled device array fiber spectrometer HR4000 (Ocean Optics, Dunedin, FL, USA) in the wavelength range of 350-550 nm during the light-curing period of 30 seconds. The data collection rate was 20 points per second. The intensity of light passing through the empty sample compartment (Teflon ring, two PET films, and two glass plates) was measured in the same manner.

Analysis of Light Transmittance Data

In order to determine the time of polymerization completeness, the light transmittance data was analyzed through the following steps:

1) Integrated intensity of the light passing through the composite sample (I_{sample}) was measured for each time point. The same procedure was done for the measurements obtained from the empty sample compartment (I_{empty}) (Figure 3a).
2) Light transmittance was calculated as the ratio I_{sample}/I_{empty}. Plotting the transmittance values vs time gives the curve shown in Figure 3b. It is known that the irradiance of dental curing units may vary with time,[21] which was also true for the two curing units in our study (Figure 2). The variability of the curing unit output was compensated for by taking into account the real-time data for I_{empty}, rather than a single averaged value.
3) The transmittance curves were trimmed to include only the part during the light curing of 30 seconds. Then the curves were scaled so that the y-values ranged from 0 to 1, the value of 1 representing the maximum transmittance at time (t) = 30 seconds (Figure 3c). This was done to present the change of transmittance on a unified scale, regardless of actual transmittance values, which are different as a result of the material composition and sample thickness.
4) The curves were fitted to the function $f(t) = y_0 + a(1-\exp(-bt)) + c^*(1-\exp(-dt))$ (Figure 3c). This function has been used previously for describing the real-time changes in monomer conversion of dental composites and was demonstrated to be applicable to the light transmittance curves as well.[22] Unlike the conversion curves where the fitting parameters a, b, c, and d reflect certain physical processes,[22] the same parameters obtained from transmittance curves are not directly related to specific physical phenomena. Detailed analysis of the individual fitting parameters in terms of underlying physical processes was not attempted in our study, as the fitting was only performed to facilitate further processing of the transmittance curves.
5) The first derivative of function f(t) from step 4 was calculated as $\Delta T(t) = df(t)/dt$. The function $\Delta T(t)$ represents the rate at which the light transmittance increases during curing (Figure 3d).

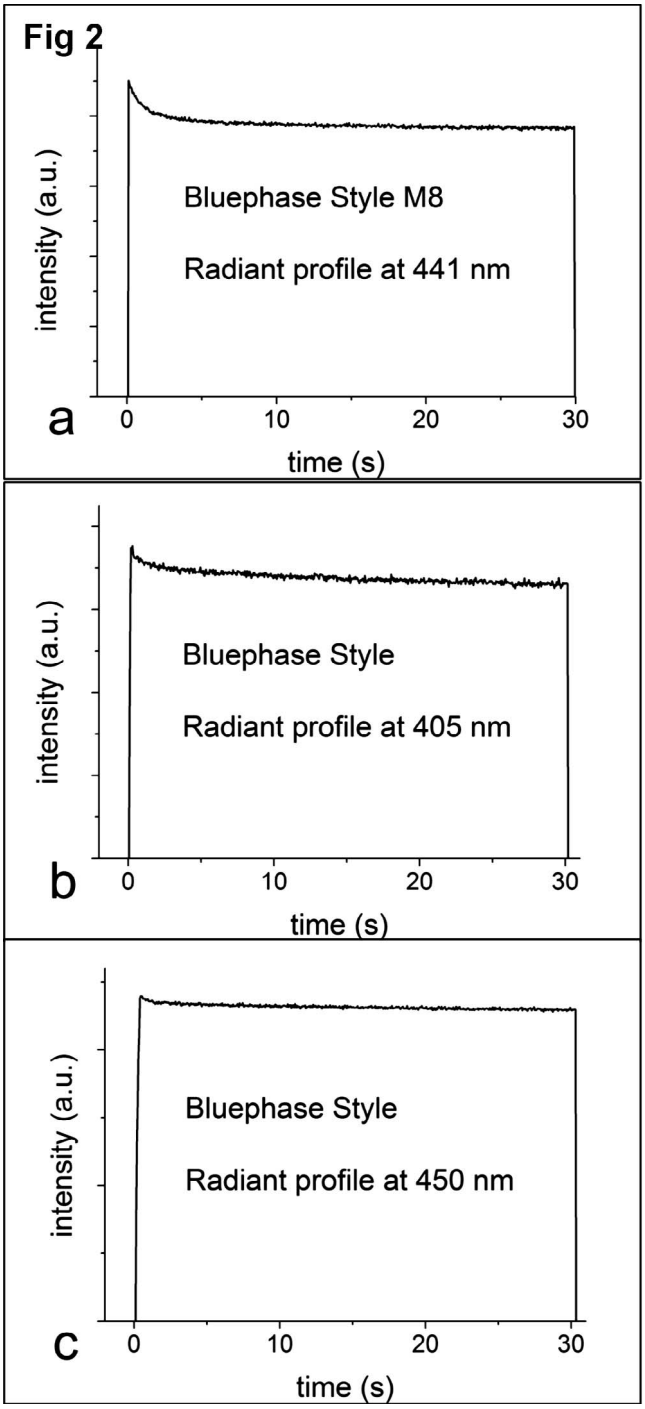

Figure 2. *Radiant profiles of the curing units Bluephase Style M8 (a) and Bluephase Style (b,c). Intensity spikes of different magnitudes are observed immediately on activation, followed by plateaus of a rather stable irradiance.*

6) From $\Delta T(t)$, the time of polymerization completeness ($t_{complete}$) was determined. As this function has no x-intercept, the polymerization was considered completed at the time when $\Delta T(t) = 0.001$ s^{-1}. The threshold value of 0.001 s^{-1} was chosen because the preliminary experiments using the approximations of first derivatives obtained from the nonfitted curves showed experimental error of this order of magnitude.
7) For some material/thickness combinations, the $\Delta T(t)$ value of 0.001 s^{-1} was not reached during the light curing of 30 seconds. In such cases, the time of polymerization completeness was determined by extrapolation [ie, plotting the function $\Delta T(t)$ beyond the 30 seconds and then finding the t value for which $\Delta T(t)=0.001$ s^{-1}]. This approach was introduced since the maximum continuous curing time supported by the curing units was 30 seconds.

Statistical Analysis

Normality of distribution was confirmed using the Shapiro-Wilk test. The mean values of light transmittance and $t_{complete}$ were compared using a three-way analysis of variance (ANOVA) with factors "material," "thickness," and "curing unit." The Tukey honestly significantly different (HSD) post hoc test was used for multiple comparisons. Partial eta-squared statistics were used to describe relative influences and interactions of the factors "material," "thickness," and "curing unit." One-way ANOVA was conducted to compare $t_{complete}$ values within a given sample thickness. The Tukey HSD post hoc test was used for the 2-mm thickness (equal variances), while the Games-Howell post hoc test was used for 4-mm thickness (unequal variances). Statistical software SPSS 20 (IBM, Armonk, NY, USA) was used, with level of significance set at 0.05.

RESULTS

Light transmittance values measured at the start and end of illumination are shown in Table 3. The group of bulk fill composites generally showed higher transmittance (2.9%-27.0%) than the conventional composites (0.7%-16.7%). The transmittance values increased during polymerization for all composites, with considerable differences in the magnitude (minimal increase of 0.2% and maximum increase of 7.0%). For a given material, curing unit, and time point, the transmittance of 4-mm-thick samples was 2 to 7.5 times lower compared to that of the 2-mm samples.

Mean values of $t_{complete}$ are given in Table 4. The shortest times (15.3-23.3 seconds) were observed for the bulk fill composites at sample thickness of 2 mm. Comparatively longer times were noted for the conventional composites at 2 mm (20.2-33.3 sec-

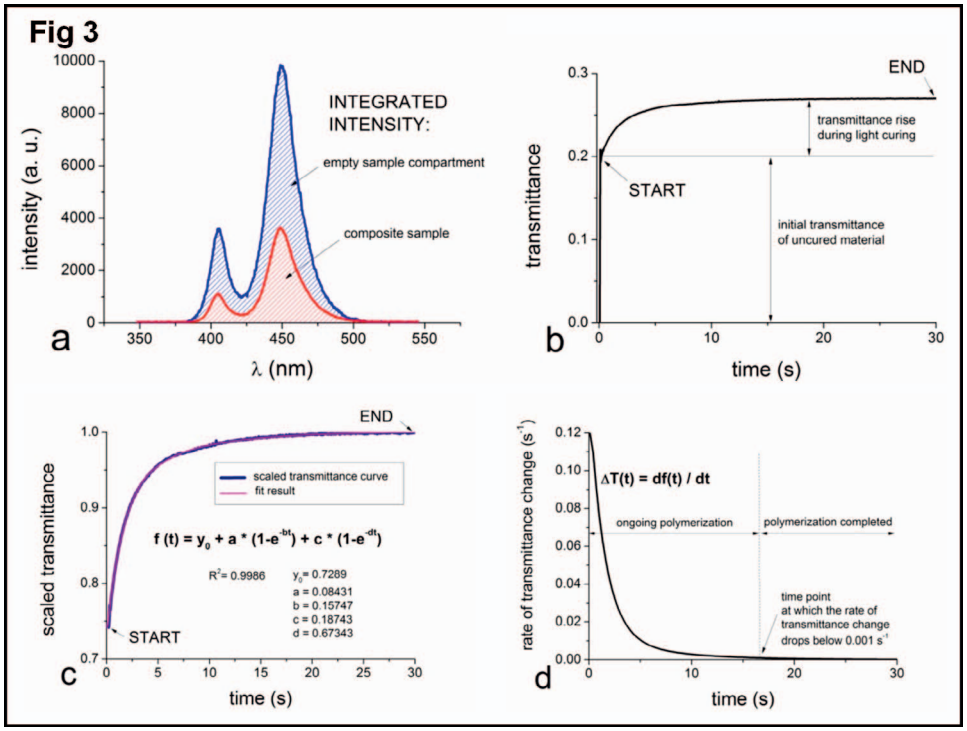

Figure 3. *An example of light transmittance analysis for a 2-mm-thick sample of material X-tra fil cured with Bluephase Style. Integrated intensities of the composite sample and the empty sample compartment (a). Light transmittance through the composite sample as a function of time (b). The points denoted as "start" and "end" are the initial and final marks for trimming the transmittance curve, respectively. The result of trimming and scaling to the y-values between 0 and 1 is shown in (c). This curve was fitted to the exponential function, whose first derivative was calculated to represent the rate of transmittance change (d). The polymerization is considered completed when the y-values of the derivative drop below 0.001 s^{-1}.*

Table 3: *Mean Transmittance Values (%). Standard Deviations Are Given in Parentheses. The Initial and Final Transmittance Values Were Determined, Respectively, at the "Start" and "End" Points of the Transmittance Curves, as Shown in Figure 3b*[a]

Composite Material	2 mm				4 mm			
	Bluephase Style		Bluephase Style M8		Bluephase Style		Bluephase Style M8	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Bulk Fill								
XF	20.85 (1.55) Aa	27.02 (1.49) Aa	13.11 (0.15) Ab	15.29 (0.11) ABb	6.87 (0.45) Ac	11.08 (0.69) Bc	5.41 (0.20) Ac	7.29 (0.19) Ad
FBF	16.26 (0.19) Ba	22.21 (0.39) Ba	7.90 (0.26) Db	9.84 (0.30) Db	4.95 (0.18) Cc	8.96 (0.50) Cc	2.95 (0.10) Ed	4.34 (0.14) Cd
TECBF-IVA	19.68 (2.19) Aa	26.70 (2.18) Aa	11.86 (0.56) Bb	14.76 (0.52) Bb	5.47 (0.12) BCc	10.65 (0.20) Bc	4.58 (0.30) Bc	7.31 (0.41) Ad
TECBF-IVB	18.33 (2.18) ABa	24.73 (1.94) ABa	12.40 (0.26) ABb	15.44 (0.28) Ab	6.06 (0.67) Bc	12.25 (0.91) Ac	4.25 (0.04) BCc	6.86 (0.07) Ad
Conventional								
TEC-A2	11.26 (1.28) Ca	15.50 (1.59) Ca	10.74 (0.31) Ca	11.85 (0.26) Cb	2.47 (0.22) Db	4.47 (0.29) Dc	3.94 (0.13) CDc	4.96 (0.26) Bc
TEC-A3	10.52 (0.23) Ca	14.80 (0.19) CDa	10.51 (0.18) Ca	11.96 (0.16) Cb	2.15 (0.23) Db	3.79 (0.43) DEc	3.59 (0.32) Db	4.43 (0.33) BCd
GDP	11.51 (0.20) Ca	16.68 (0.57) Ca	6.99 (0.41) Eb	8.51 (0.33) Eb	2.40 (0.19) Dc	4.36 (0.39) DEc	0.93 (0.07) Fd	1.62 (0.12) Dd
GR	9.81 (0.42) Ca	11.79 (0.46) Da	3.05 (0.15) Fb	3.55 (0.18) Fb	2.44 (0.15) Dc	3.25 (0.20) Eb	0.68 (0.04) Fd	0.89 (0.04) Ec

[a] *Same uppercase letters denote statistically similar values within a column. Same lowercase letters denote statistically similar values within a row for a given time point (initial/final).*

Table 4: *Times Required for a Complete Polymerization, Mean (SD)*

Composite Material	2 mm		4 mm	
	Bluephase Style	Bluephase Style M8	Bluephase Style	Bluephase Style M8
Bulk Fill				
XF	15.29 (1.12)	16.19 (0.80)	26.94 (0.73)	31.78 (1.36)
FBF	17.64 (1.21)	22.42 (0.74)	31.54 (1.55)	38.28 (0.68)
TECBF-IVA	20.85 (1.04)	23.32 (1.13)	39.10 (0.53)	42.05 (1.87)
TECBF-IVB	18.39 (2.31)	21.28 (0.80)	36.08 (1.36)	41.38 (0.66)
Conventional				
TEC-A2	22.09 (2.42)	22.08 (2.90)	40.90 (3.80)	49.03 (4.03)
TEC-A3	20.15 (0.82)	24.66 (2.56)	56.33 (12.88)	40.05 (8.71)
GDP	26.32 (2.80)	28.20 (0.80)	59.78 (4.75)	N/A
GR	33.25 (0.81)	N/A	56.70 (8.64)	N/A

Abbreviations: N/A, not available.

onds), followed by the bulk fill composites at 4 mm (26.9-42.1 seconds), and finally the conventional composites at 4 mm (40.1-59.8 seconds). As a result of the poor signal/noise ratio and subsequently high data scatter (coefficients of variation up to 100%) for three material/thickness/curing unit combinations, the corresponding data are considered unreliable and are not reported in Table 4. Mean values of $t_{complete}$ are additionally represented graphically and complemented with the results of the statistical analysis in Figure 4. This is convenient for visualizing the differences among the materials, sample thicknesses, and curing units.

Table 5 reports relative contributions of the factors "material," "thickness," and "curing unit" on the light transmittance and $t_{complete}$. All of the factors exerted a highly significant influence on the dependent variables, whereas "thickness" and "material" proved more influential than "curing unit." Also, a significant interaction was observed for all factor combinations.

DISCUSSION

This work investigated the light transmittance of dental composites and assessed the real-time light transmittance monitoring as a means for determining curing times required for a complete polymerization.

Effect of Composite Material, Sample Thickness, and Curing Unit on Light Transmittance

The first hypothesis was accepted, as the light transmittance was significantly affected by factors "material," "thickness," and "curing unit" (Table 5). The greatest influence was observed for the factor "thickness," which can be explained by the well-known exponential increase of light attenuation with lengthening of the light path through the composite.[15,16] The values of light transmittance varied greatly among the composites (Table 3). This was caused by differences in filler type, load, and geometry, as well as by different resin compositions

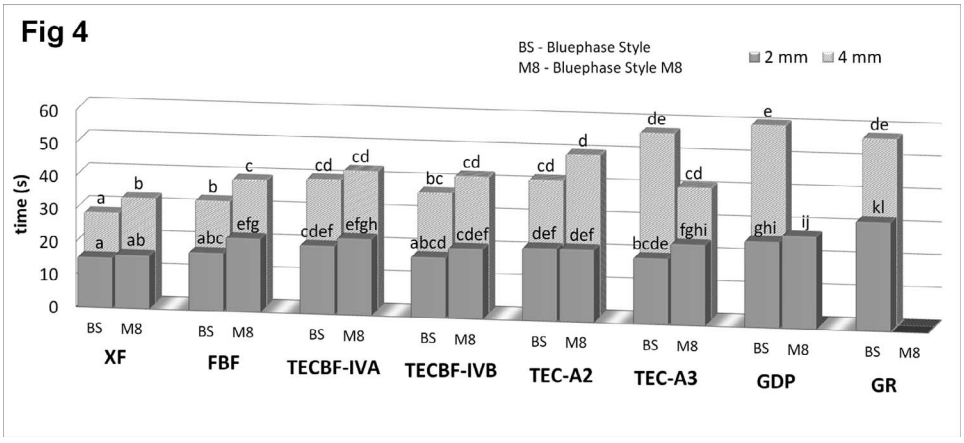

Figure 4. *Time required for a complete polymerization and results of the statistical analysis. Same lowercase letters denote statistically similar groups within an individual layer thickness. The three missing bars represent the data not available.*

Table 5: *Influence of the Factors Thickness, Material, and Curing Unit and Their Interactions on the Initial and Final Transmittance Values and Time of Polymerization Completeness*

Factor	Initial Transmittance		Final Transmittance		Time of Polymerization Completeness	
	p	Partial η^2	*p*	Partial η^2	*p*	Partial η^2
Thickness	<0.001	0.973	<0.001	0.977	<0.001	0.966
Material	<0.001	0.925	<0.001	0.960	<0.001	0.918
Curing unit	<0.001	0.821	<0.001	0.936	<0.001	0.625
Thickness × material	<0.001	0.645	<0.001	0.617	<0.001	0.352
Material × curing unit	<0.001	0.702	<0.001	0.768	0.005	0.231
Thickness × curing unit	<0.001	0.709	<0.001	0.802	0.004	0.112

and pigment additives.[23] When considered as a group, the bulk fill composites presented higher transmittance values (2.9%-27.0 %) than did the conventional composites (0.7%-16.7%). This is a common feature of bulk fill composites[2] and is necessary for their bulk fill capability.

As the light scattering at filler particles is the main determinant of light transmittance, one could expect the decrease of transmittance with increasing filler load.[24] However, in our study no relationship between transmittance and filler load was found, since the transmittance was considerably influenced by other factors, mainly filler geometry and filler/resin refractive index mismatch. Thus, filler load alone was not a good predictor of light transmittance. This can be illustrated by the fact that the least translucent material (Grandio) and the most translucent material (X-tra fil) had similar filler loads of 71 vol% and 70 vol%, respectively. This difference in transmittance can be attributed to the Grandio particle size of 0.1-2.5 μm[25] causing much higher scattering of blue light[16] than was caused by the comparatively larger 2-3-μm particles contained in X-tra fil.[25] An additional interesting observation is that X-tra fil showed the highest light transmittance despite being among the most highly filled materials in our study (Table 1), demonstrating that high filler load is not necessarily incompatible with the bulk fill capability.

When comparing the light transmittance values between the two polymerization devices with all other factors being equal, transmittance was generally higher in the case of Bluephase Style (Table 3). The transmittance of dental composites is mainly determined by light scattering,[14] which is in turn dependent upon the wavelength of incident light, geometry of the filler particles, and mismatch of the refractive indices between the filler and resin.[16] As the detailed composition of commercial composites is undisclosed by the manufacturers, insufficient data are available on the particle geometry and refractive indices of individual fillers and monomer blends. Thus, the observed difference in transmittance between two curing units cannot be thoroughly discussed. It can only be speculated that the consistently higher light transmittance for Bluephase Style was due to the differences in the radiant spectra of the curing units: namely, as the intensity of light scattering is inversely related to the wavelength,[15] the light produced by Bluephase Style (major radiant peak at 450 nm) may have been less scattered than that produced by Bluephase Style M8 (single radiant peak at 441 nm) (Figure 1).

All of the composites showed an increase in light transmittance during light curing (Table 3). The individual combinations of material/thickness/curing unit showed large differences in the amount of transmittance increase. For example, transmittance of 2-mm samples of Tetric EvoCeram (shade A2) cured with Bluephase Style M8 increased for a factor of 0.1, while for the 4-mm samples of Tetric EvoCeram Bulk Fill (shade IVB) cured with Bluephase Style, transmittance increased for a factor of 1.0. . The factors, for which the light transmittance was increased in the other composites, ranged between these two extreme values. A practical implication of the transmittance rise during curing is that the gradual improvement of curing light penetration can enhance the radiant energy received by the bottom of the overly thick layers that sometimes occur in clinical practice. These layers are commonly undercured; however, a considerable increase of transmittance during polymerization might help to mitigate the undercuring, provided that sufficiently long curing times are used. In this regard, the composites whose transmittance increases for a larger factor may benefit more from extended curing[7] and be more successful at avoiding the undercuring of accidentally placed layers of excessive thickness.

Real-time Light Transmittance Monitoring as a Means for Determining Polymerization Completeness

The rate of transmittance change was presented as a function of time, and values above 0.001 s^{-1} were considered to indicate an ongoing polymerization. As the rate of transmittance change fell below this threshold, the polymerization was considered complete, and times at which this occurred were denoted as $t_{complete}$ (Figure 3d). Although the light transmittance increased during curing for all of the tested composites, a different transmittance behavior is possible. For example, one recently launched bulk fill material shows an increase in light transmittance during polymerization.[26] Also, by tuning the filler/resin refractive indices, composites could be formulated with the same initial and final refractive index mismatch, so that their initial and final transmittances correspond.[27] Both mentioned behaviors should be compatible with the presented method of assessing polymerization completeness, as this method relies only on the light transmittance change, regardless of its direction and absolute transmittance values.

The presented method showed some limitations, as observed for the 4-mm samples of conventional composites, the $t_{complete}$ values for which amounted to 40.1-59.8 seconds. Since the curing lasted for 30 seconds, the $t_{complete}$ values longer than this time were estimated by extrapolation. The extrapolation approach is inherently inaccurate, and higher inaccuracy is expected for values that are farther away from the measured range. This explains the highest scatter of $t_{complete}$ data for 4-mm-thick samples of conventional composites among all other material/thickness combinations, as their $t_{complete}$ is rather remote from the measured range of 0-30 seconds. Overall, it appears that our method gives reproducible results for $t_{complete}$ values that are contained within the time interval of curing unit activation, as well as for extrapolated estimates up to about 40 seconds. Estimates of $t_{complete}$ higher than 40 seconds featured high scatter and mostly related to the 4-mm-thick samples of conventional composites. These estimates are, however, of little clinical relevance, as conventional composites are not intended for placement in 4-mm-thick layers.

Another limitation of our method is poor reproducibility when low transmittance rises during polymerization (below 0.7%) were coupled with low transmittance values (0.7%-3.6%), which yielded low signal to noise ratio and consequently high coefficients of variability (above 100%). This was the case for the three cells in Table 4 whose values were denoted as not available. An additional aspect of multifunctional methacrylate polymerization that is not accounted for by our method is the phenomenon of postcure reaction. As a result of an immense increase in viscosity of a reaction medium during polymerization, the mobility of reactive species is impaired and polymerization rate decreases substantially.[28] Thus, a high proportion of monomer remains unreacted and available for further polymerization, which is known to slowly continue for at least 24 hours after light curing.[29] In this regard, our method of determining polymerization times is limited to the changes that occur during the light curing and does not account for the reaction that occurs thereafter. Although the postcure increase in monomer conversion can be rather extensive[30] and may compensate for the initially lower conversions attained during a short period of light curing,[31] it would be beneficial to attain as high a rate of conversion as possible during light curing in order to minimize the toxic potential of unreacted monomer.

The partial eta-squared statistics showed that factors "material," "thickness," and "curing unit" exerted a significant influence on $t_{complete}$, whereas significant interactions between the factors imply that the influence of each individual factor depended on the level of other factors (Table 5). These findings support the second hypothesis and reflect the fact that the polymerization kinetics, and consequently the values of $t_{complete}$, depend upon a complex interplay of multiple factors, some of which are sample geometry, total irradiance and spectral irradiance of the curing unit, monomer viscosity and reactivity, filler load and particle size distribution, photoinitiator type, reactivity, and concentration.[23,32,33] However, it is interesting to note that the $t_{complete}$ could be rather well described as a function of the single parameter (ie, light transmittance). This is demonstrated in Figure 5, which plots $t_{complete}$ as a function of light transmittance and supports our third hypothesis. Although it is obvious that $t_{complete}$ should be inversely related to light transmittance, the fact that their relationship could be well fitted to an exponential function suggests that transmittance was the major determinant of the curing time needed for a complete polymerization, while the other variables appear to play a comparatively smaller role. Since the light transmittance was highly influenced by the factor "thickness," it is understandable that the same factor also exerted the highest influence on $t_{complete}$, as shown by the corresponding partial eta-squared values in Table

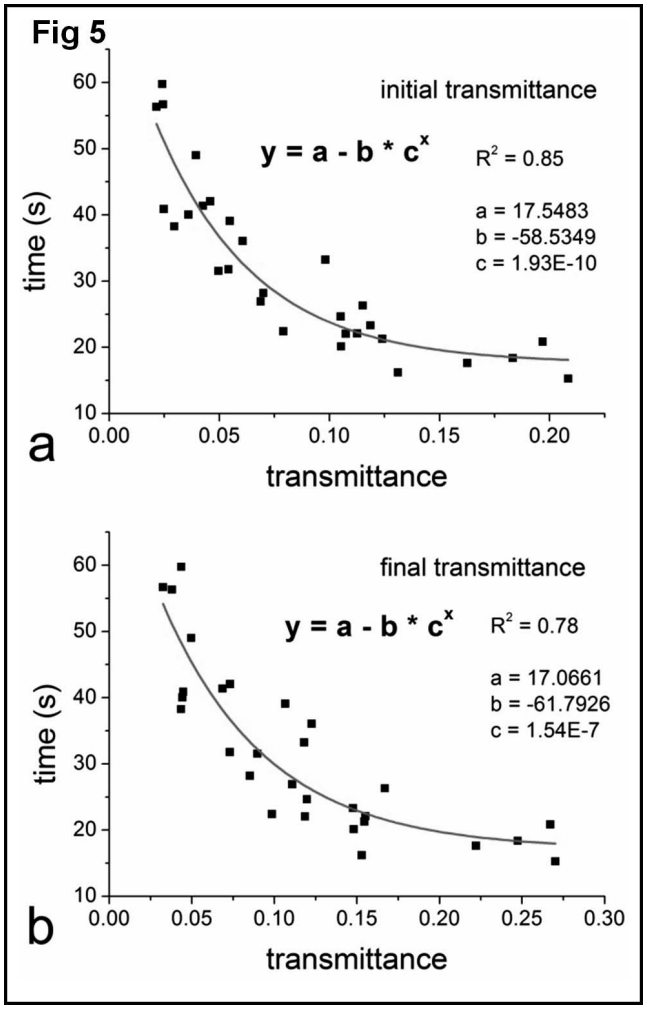

Figure 5. *Relationship between the light transmittance and time of polymerization completeness. The initial ("start" from Figure 3b) and final ("end" from Figure 3b) transmittance values were plotted against the time required for a complete polymerization. Each point represents a single combination of material/thickness/curing unit and is a mean value of n = 4.*

5. Finally, the finding that polymerization completeness highly depends on the layer thickness emphasizes the need to strictly follow recommendations on maximum layer thickness in clinical work.

Curing unit Bluephase Style M8 was recently introduced to the market as an economic alternative to its more expensive counterpart, Bluephase Style. The latter features a wider radiant spectrum (Figure 1), which is favorable for curing composites containing alternative photoinitiators[34]; however, the large majority of available composites are camphorquinone-initiated[35]; hence, such wide spectrum is not necessary. This was the rationale for launching Bluephase Style M8 as a curing unit of a more favorable price/performance ratio.[36] In line with its lower irradiance, Bluephase Style M8 showed curing efficiency that was inferior to that of Bluephase Style, evidenced by the longer $t_{complete}$ values (Table 4; Figure 4). This may be explained by the following characteristics of Bluephase Style: 1) better light penetration through composite materials (Table 3); 2) higher total light irradiance (Table 2), which activates more photoinitiator molecules while also improving resin mobility due to the temperature rise[37]; and 3) major radiant peak closer to the maximum absorption of camphorquinone at 468 nm (Figure 1).[38]

Among the composites in our study, only Tetric EvoCeram Bulk Fill contained an alternative photoinitiator Ivocerin, in addition to the conventional camphorquinone-amine photoinitiator system.[26] Ivocerin is a patented germanium-based compound that is claimed to improve the curing efficiency of thick layers because of its high reactivity at low irradiance.[11] From the data on 4-mm-thick samples of bulk fill composites, the benefit of Ivocerin could not be confirmed, as Tetric EvoCeram Bulk Fill required similar or longer $t_{complete}$ than the camphorquinone-initiated material Filtek Bulk Fill (Figure 4), despite lower light transmittance of the latter (Table 3). The 4-mm values of $t_{complete}$ for Tetric EvoCeram Bulk Fill were also higher than those of another camphorquinone-initiated bulk fill composite, X-tra fil, which can be explained by differences in light transmittance (Table 3; Figure 4).

The composites Tetric EvoCeram and Tetric EvoCeram Bulk Fill were tested in two shades (Table 1). The different shades of the same material are compositionally very similar and differ only in the small amount of pigments. These subtle compositional variations did not cause a statistically significant difference in transmittance values between two shades, nor did they have an impact on the values of $t_{complete}$ (Table 3; Figure 4).

Composite manufacturers commonly provide instructions for use that specify the minimum irradiance and curing time required for curing of an individual layer (Table 1). These data apply to the standard layer thickness of 2 mm for conventional and 4 mm for bulk fill composites. Some manufacturers also suggest that curing times could be shortened if a curing unit of sufficient irradiance is used. Thus, for some of the composites, curing times as short as 10 seconds are recommended. Although certainly attractive from a clinical standpoint, short curing times may yield an incomplete polymerization and compromise multiple restoration properties.

Tarle and others[6] examined five bulk fill composites cured with an LED curing unit with irradiance

of 1170 mW/cm^2 and found suboptimal values of monomer conversion and microhardness when 4-mm-thick samples were cured according to the manufacturer's recommendations. They also found that mechanical properties of cured bulk fill composites can be improved by prolonging the curing times up to 30 seconds. A similar investigation was conducted by Zorzin and others,[7] who used irradiance of 1200 mW/cm^2 to compare the effect of 30-second curing time with the manufacturer-recommended curing times of 10-20 seconds. In their study, the extended curing for 30 seconds resulted in improved hardness and monomer conversion for several bulk fill composites and the conventional reference material. Moreover, Miletic and others[39] determined optimal curing times by assessing monomer conversion and hardness of bulk fill composites cured with LED unit of 1100 mW/cm^2 and showed that for the low-viscosity (flowable) bulk fill composites, a curing time of 10 seconds was sufficient, whereas high-viscosity (sculptable) bulk fill composites required at least 20 seconds. Other studies on bulk fill composites that assessed the effect of various curing protocols on layers up to 6 mm were performed by Ilie and Stark[11,40] and reported the value of 23.5 J/cm^2 as the minimum radiant energy required for a sufficient polymerization, which corresponds to 20 seconds of curing with irradiance of 1176 mW/cm^2. Our work used curing units of lower irradiances (658 and 938 mW/cm^2) than the cited studies,[6,7,11,39,40] which resulted in comparatively longer curing times needed for a complete polymerization (20.2-33.3 seconds for 2-mm layers of conventional composites and 26.9-42.1 seconds for 4-mm layers of bulk fill composites). In summary, all of these results contribute to a considerable amount of evidence suggesting that short curing times of 10-20 seconds, as recommended by some manufacturers, are insufficient for optimal polymerization, even under ideal curing conditions in the laboratory setting. The fourth hypothesis was thus rejected.

Clinicians tend to use longer curing times than those minimally recommended by composite manufacturers as a means of avoiding a possible undercuring.[41] The commonly used curing times are preset in the contemporary curing units and range from 10 to 40 seconds, whereas the longest "program" of 40 seconds exceeds by far the recommendations of composite manufacturers (Table 1). Our results show that the longest curing setting of Bluephase Style and Bluephase Style M8 (30 seconds) ensured an adequate cure of 2-mm layers for all of the tested composites, except for Grandio, whose $t_{complete}$ was 33.3 seconds (Table 4). This can be attributed the fact that Grandio had the lowest transmittance among all of the materials (Table 3). For 4-mm-thick layers, the curing time of 30 seconds ensured a complete polymerization only for material X-tra fil, whereas all other composites required longer curing times. These data suggest that in the clinical work most of the investigated bulk fill composites placed in 4-mm layers would require more than one curing cycle of 30 seconds in order to reach complete polymerization.

It should be noted that the manufacturer recommendations are based on ideal-case laboratory studies, which rarely correspond to a more complex clinical reality. Delivering the sufficient radiant energy to the restorations in clinical practice is often hindered by the distance and angulation of the curing unit tip. Most of the parameters related with the curing effectiveness (true irradiance and its decrease due to the curing unit aging, light beam inhomogeneity, spectral irradiance and its effect on particular photoinitiators) are unknown to clinicians, while some factors (position of the curing unit relative to the restoration) are beyond their control. However, most of these issues could be to some extent mitigated by prolonged curing,[6,7] once again highlighting the benefit of extending the curing times beyond those recommended by the manufacturers.

CONCLUSIONS

Within the limitations of this study, the following can be concluded:

1) The real-time light transmittance monitoring can be used as a simple and effective means for assessing the time required for a complete polymerization of dental composites;
2) Sample thickness was the most influential factor for the time of polymerization completeness, followed by the factors material and curing unit;
3) Time of polymerization completeness showed an exponential relationship with the light transmittance; and
4) The times required for a complete polymerization under clinically relevant curing conditions (layer thickness of 2 mm for conventional and 4 mm for bulk fill composites) ranged from 15.3 to 42.1 seconds, which considerably exceeds some of the curing times recommended by the manufacturers.

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Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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