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# Effect of thickness and irradiance on the polymerization delay at the bottom surface of light-cured resin composites

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ABSTRACT

*Objective:* To examine the effects of the resin-based composite (RBC) thickness and incident irradiance on the time delay after the light turns on before polymerization starts at the bottom surface of the RBC.

*Methods:* The degree of conversion (DC) was determined using Fourier-transform infrared spectroscopy (FT-IR) at a rate of 13 measurements per second. Six commercial RBCs were tested at three thicknesses (0.2, 2 and 4 mm) and four incident irradiance values (472–3985 mW/cm$^2$).

*Results:* There was a significant time delay before polymerization began at the bottom of each RBC. At 942 mW/cm$^2$, representative of many current LCUs, this delay ranged from 0.12 to 1.11 s at the bottom of 2 mm of RBC. When the thickness was increased to 4 mm, even with an irradiance of 1969 mW/cm$^2$, which represents high-power LCUs, the delay ranged from 0.12 to 5.17 s. The highest irradiance of 3985 mW/cm$^2$ did not fully overcome the inherent lag caused by the thickness of the RBC. At 3985 mW/cm$^2$, PowerFlow and PowerFill had the shortest delay times of 0.09 s and 0.30 s, respectively, at the bottom of a 4 mm thick RBC.

*Significance:* The presence of a time delay before photo-cured RBCs start to polymerize at the bottom surfaces must now be addressed clinically and when calculating reaction rates.

## 1. Introduction

Most contemporary resin-based composite filling materials (RBCs) are photoactivated using blue light from a light-emitting diode (LED) light-curing unit (LCU) [1,2]. Most resin manufacturers recommend delivering at least 500 mW/cm$^2$ to their resin-based composites (RBCs), but some state that irradiances up to 3300 mW/cm$^2$ can be used [3–8].

When choosing which LCU to purchase, dentists consider high irradiance the second most important feature after portability [9] because of claims that a high irradiance will offer the clinician the ability to save time and money [1]. The development of high-power LED LCUs has led some manufacturers to claim that adequate photoactivation can be achieved using short exposure times of 1–3 s [10–12] based on the assumption that there is exposure reciprocity between irradiance and exposure time [1,2,13,14]. The higher the irradiance, the less time required to photocure the RBC. However, most studies report that fast photocuring is inadvisable [15–24], and it has become important to examine the behaviour of RBCs during the first few seconds of light exposure, not just at the end.

The optical properties of photocuring RBCs are affected by refractive index shifts associated with the degree of conversion (DC), transient thermal variations due to the reaction exotherm, and radiative heating from the LCU [25]. Ivoclar claims that its Tetric PowerFill and Tetric PowerFlow RBCs include ‘Aessencio’ technology [10] and will allow more light to reach the bottom of these products in the first few seconds of exposure, after which the RBCs become more opaque. The manufacturer of Filtek One bulk-fill (Solventum/3 M Oral Care) claims to manage the interaction and refractive index change, by allowing for

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increased opacity without sacrificing depth of cure [26]. They claim that due to a deliberate mismatch in the refractive index of the resin and the filler, their uncured material is more translucent than the cured paste, allowing more light to penetrate deeply and thus providing a greater depth of cure [26].

### 1.1. *Why a time delay before polymerization starts should be expected*

Treating polymerization as if it starts immediately the LCU turns on is inconsistent with the fundamental behaviour of the inhibitors present. These inhibitors must first be consumed before the free radicals generated by the photoinitiator effectively initiate polymerization. Additionally, dissolved oxygen is also present, and this also acts as an inhibitor [27]. Thus, there must always be some delay before polymerization starts, no matter how small .

Until most of the inhibitors have been consumed, there can be no polymerization because the free radicals that are first produced, whether primary initiating radicals or propagating radicals on growing polymer chains, are preferentially consumed by these highly-reactive competitors. Their consumption rate depends on the local irradiance within the RBC, which decreases exponentially from its surface [1,2,28–30]. The time lag before productive polymerization begins will be longer at lower local irradiance levels, and the reaction rate should decrease with depth [1,2,28–30] because it takes more time to produce enough ‘sacrificial’ radicals. These sacrificial radicals react with and cause a decrease in the concentration of both the inhibitor and oxygen to levels where radical addition to the monomer and thus chain propagation become dominant, and photopolymerization effectively begins. The time delay may be somewhat modified by the photobleaching effect [1,2] that occurs as the initiator is reacted: the blue light is less absorbed, thus allowing more to be transmitted deeper into the RBC.

### 1.2. *Current status when measuring the polymerization kinetics of RBCs*

While light from the LCU reaches the bottom of a 4-mm thick increment effectively instantaneously (given the speed of light), this does not mean that the polymerization reaction at the bottom starts immediately. Although emerging technologies have enabled faster data collection, treating polymerization as if it were to begin immediately throughout all of the RBC as soon as the LCU turns on remains prevalent [15,20,31–39]. Several recent studies have the same data-collection problems. One recorded data every 0.4 s during fast (3-s exposure) photopolymerization [32]; another recorded data every 2 s to determine the maximum polymerization rate and the time to achieve it [33]; one study using a blue laser collected data at a rate of 2 spectra/s [15]; a study of the polymerization rate in low-viscosity RBCs used data recorded every 5 s [37]. Each of these studies defined time zero as the moment when the LCU was turned on and analyzed the data as if polymerization started immediately, because the equipment used to collect ’real-time’ data could not record data fast enough to determine when polymerization began at the bottom surface [31–33,35,37,39]. In addition, most conclusions have been drawn using curve-fitting and have used exponential fitting functions that were constrained to start when the LCU was turned on, *i.e.* at zero seconds [15,20,31–35,37,39]. While this aspect may not be significant if the purpose is to report the final DC, if the study aims to document reaction kinetics as a function of cure depth, or investigate the effects of short exposure durations on polymerization kinetics, then any delay before polymerization starts is relevant. Using higher data collection rates, such as ~0.08 s/scan [40–42], it has been reported that the time delay before photopolymerization starts at the bottom of the RBC increases as the thickness increases, or the irradiance decreases [41]. Reported delays were less than 0.077 s for 0.2 mm-thick samples of PowerFill (Ivoclar) irradiated at 3000 mW/cm$^2$, while the time delays at a depth of 4 mm ranged from 0.59 s when 1000 mW/cm$^2$ was delivered, to 0.23 s at 3000 mW/cm$^2$.

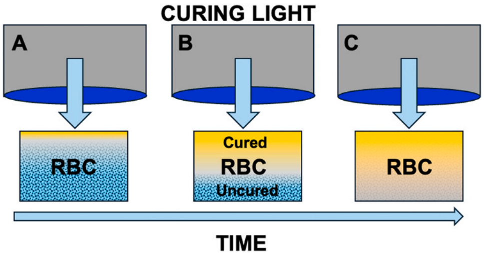

**Fig. 1.** Schematic illustrating how incident light reaches the bottom at time 0 s (A, light blue), but the polymerization reaction (light yellow) takes time (B and C) to start at the bottom of the RBC.

### 1.3. *Clinical relevance of determining the delay*

Knowing that the RBCs exhibit significant delays before the reaction starts at the bottom of the restoration would inform clinicians of the appropriateness of using shorter exposures, particularly in deep restorations. If the bottom layer only begins to polymerize near the end of a short light exposure, there will likely be inadequate curing. Thus, clearer guidelines for optimal light-curing practices could be established by quantifying how the thickness, irradiance and optical properties influence the initiation time at the bottom of a wider variety of paste- and flowable-consistency RBCs.

### 1.4. *Purpose*

Given the above, a wider range of RBCs was examined under clinically-relevant conditions than previously reported [41,42]. What was to be established was:

- Confirmation that a time delay exists between activation of the LCU and when conversion is first detected at the bottom of the RBC;
- Quantification of the effect of RBC thickness and irradiance delivered on this delay;
- Documentation of the variation between RBCs with a view to clinical guidance on the effects of exposure time, RBC thickness and irradiance delivered.

## 2. Materials and methods

### 2.1. *Outline*

To determine when polymerization starts at the bottom surface, the DC was recorded in real-time at a high temporal resolution [41] rate of approximately 13 measurements per second (*i.e.,* every 0.077 s) using attenuated-reflectance (ATR) Fourier-transform infrared spectroscopy (FT-IR). Six commercially-available RBCs – four high-viscosity sculptable and two flowable (Table 1) – were examined. Each could be activated by light at 447 nm [3–8]. Three thicknesses (0.2 mm – effectively approximating the top, irradiated surface, 2 mm, and 4 mm) were exposed at four irradiances (Table 2), covering the range of manufacturer-accepted values (Table 1).

### 2.2. *Polymerization light source*

A standard LCU (Bluephase G4; Ivoclar, Schaan, Liechtenstein) was modified by the manufacturer to allow the blue and violet LEDs to be connected separately to a programmable power supply (GW Instek GPP-2323; Instek America, Montclair, CA, USA). Only the blue LED emitters were activated to avoid complications caused by the differences in the absorption of violet compared with blue light [28,29]. The irradiance values used (Table 2) were obtained by adjusting the output from the power supply, noting that the 942 and 1959 mW/cm$^2$ values covered the output of many contemporary LCUs. Only the determination of the

**Table 1**
RBC materials used, the manufacturer-recommended [3–8] maximum increment, and exposure time. irradiance and appropriate wavelength ranges.

| RBC | Consistency, type, max. increment | Manufacturer (lot number) | Shade | Recommended exposure time, irradiance, wavelength range |
|---|---|---|---|---|
| Filtek Bulk Fill Flowable | Flowable,<br>bulk-fill<br>4 mm | Solventum/3 M Oral Care<br>(9731521) | A2 | 40 s at 550–1000 mW/cm$^2$<br>*or*<br>20 s at 1000–2000 mW/cm$^2$<br>400–500 nm |
| Tetric PowerFlow | Flowable,<br>bulk-fill<br>4 mm | Ivoclar<br>(Z062V1) | IVA | 20 s at 500–900 mW/cm$^2$<br>*or*<br>3 s at 2700–3300 mW/cm$^2$<br>400–500 nm |
| Filtek One Bulk Fill | Sculptable,<br>bulk-fill<br>4 mm | Solventum/3 M Oral Care<br>(9760334) | A2 | 40 s at 550–1000 mW/cm$^2$<br>*or*<br>20 s at 1000–2000 mW/cm$^2$<br>400–500 nm |
| Tetric PowerFill | Sculptable,<br>bulk-fill<br>4 mm | Ivoclar<br>(Z02TWW) | IVA | 20 s at 500 – 900 mW/cm$^2$<br>*or*<br>3 s at 2700–3300 mW/cm$^2$<br>400–500 nm |
| Admira Fusion x-tra | Sculptable,<br>bulk-fill<br>4 mm | Voco Dental<br>(2150141) | U | 20 s at 800 mW/cm$^2$ LED or halogen light |
| TPH Neo Spectra ST-LV | Sculptable,<br>conventional<br>2 mm | Dentsply Sirona<br>(2309000420) | A3 | 20 s at 550–799 mW/cm$^2$<br>440–480 nm |

**Table 2**
Mean ± standard deviation (s.d.) exposure conditions delivered to the 6 mm-diameter RBC test pieces (n = 3).

| Irradiance (mW/cm$^2$) mean ± s.d. | Exposure duration / s |
|---|---|
| 472 ± 2 | 40 |
| 942 ± 2* | 20 |
| 1959 ± 5 | 10 |
| 3985 ± 51 | 5 |

* Matched to the output in the blue wavelength region from an unmodified Bluephase G4 LCU.

time delay before polymerization started at the bottom of the RBCs was of interest.

To verify consistent LCU performance throughout the experiment, the irradiance was measured before and after the study using a 6-inch integrating sphere (Labsphere; North Sutton, CT, US) connected to a spectrometer (Flame USB; Ocean Optics, Orlando, FL, US). The integrating sphere entrance aperture was restricted to 6 mm to equal the diameter of the RBC test pieces; the power value recorded was thus the same as that at the top surface of the RBC. The LCU light guide tip was fixed at the entrance to the integrating sphere. A reference value for the supply voltage was set to match the output from an unmodified Bluephase G4, which provided a blue light irradiance of 942 mW/cm$^2$ when measured through the same 6-mm aperture into the sphere. Note that this irradiance value did not include the light emitted in the violet range (<420 nm).

Representative emission spectra delivered from the modified LCU at the four irradiance values are shown in Fig. 2 based on factors of × 0.5, × 1, × 2 and × 4 of a standard 20-s exposure duration at ~1000 mW/cm$^2$. The resulting irradiances covered the irradiances recommended by the manufacturers of the RBCs (Table 1).

### 2.3. Degree of conversion (DC) data collection

The degree of monomer conversion (DC) was calculated using time-based, mid-infrared (mid-IR) absorption spectra of the RBC test pieces. Data were collected in real time using an FT-IR spectrometer (Vertex 70; Bruker, Billerica, MA, USA) with a temperature-controlled ATR attachment (Golden Gate; Specac, Orpington, Kent, UK). An optical filter (F311-H; Bruker) was used to eliminate wavenumbers above 2000 cm$^{-1}$, thereby reducing aliasing artifacts and improving the signal-to-noise ratio. The temperature of the ATR plate was set at 32 °C, which is similar to the nominal *in vivo* tooth preparation surface temperature [43]. Spectrometer scans were obtained using a 'double-sided' method whereby the mirror executed a forward and backward movement, recording a spectrum in each direction between 750 and 2000 cm$^{-1}$ at a resolution of 8 cm$^{-1}$. An average of the forward and backward spectra was used to calculate the DC.

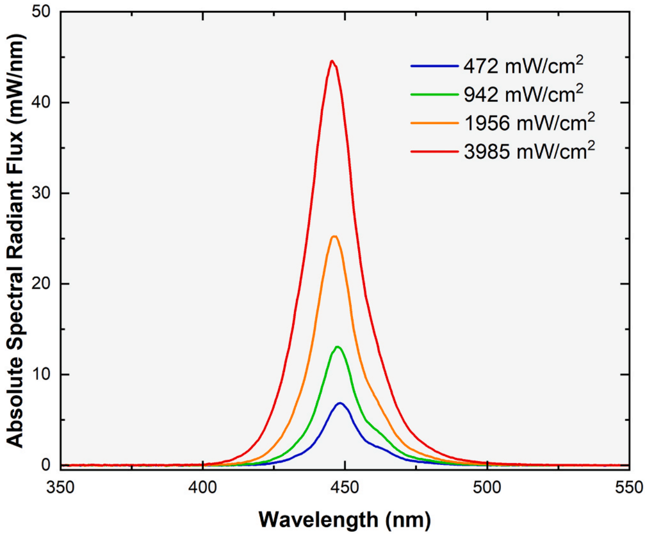

**Fig. 2.** Spectral radiant flux and irradiance (mW/cm$^2$) from the modified LCU. The 942 mW/cm$^2$ matched the blue wavelength output (peak emission at 447 nm) from an unmodified Bluephase G4 LCU.

A photodetector was placed next to the RBC on the ATR accessory to detect when the LCU was turned on. Before data collection began, 50 scans of the uncured RBC were collected and averaged to serve as the reference spectrum for the subsequent DC calculation. The spectrometer was programmed (OPUS 8.5.29 software; Bruker) to automatically start collecting data at a rate of ~13 forward and backward scans per second at the same time the LCU was turned on. Data were collected for 12 min, but because the purpose of this study was to investigate the time delay before the DC started to change at the bottom of the RBC, only the first 60 s are reported.

The start of resin polymerization was calculated in one of two ways, depending on the composition of the RBC. For the 4 RBCs having an aromatic ring (*i.e.* all except Admira Fusion x-tra and Filtek One), the DC was calculated by comparing the spectral peak absorption height, *H(t),* taken from when the LCU turned on, for the aliphatic methacrylate (C=C) peak (1635 $\text{cm}^{-1}$) with that of an aromatic absorption peak (1609 $\text{cm}^{-1}$), both being normalized with respect to their heights, *H(0)*, in their respective reference spectra, and then taking the ratio of these two values. Thus, to calculate DC, the following formula was used:

$$DC(t) = 100\,\%\cdot\left(1 - \left(\frac{H(t)_{1635polymerized}/H(t)_{1609polymerized}}{H(0)_{1635unpolymerized}/H(0)_{1609unpolymerized}}\right)\right) \quad (1)$$

Because Admira Fusion x-tra and Filtek One did not have an aromatic peak, the DC of these products was calculated using the ratio of the height of the aliphatic C=C peak (1635 $\text{cm}^{-1}$) over time to its height in the reference (unpolymerized) spectrum:

$$DC(t) = 100\,\%\cdot\left(1 - \left(\frac{H(t)_{1635polymerized}}{H(0)_{1635unpolymerized}}\right)\right) \quad (2)$$

For both, a baseline was determined in software (Opus, Bruker), from which the heights of the absorption peaks were measured.

### 2.4. Test piece preparation

To reduce operator-related variability and the risk of bias, the RBC test pieces were fabricated in a batch, but in random order with respect to thickness and irradiance. Three test pieces for each condition (3 thicknesses × 4 irradiances × 3 repeats = 36 per product) were prepared by packing the RBC directly into a mold on the ATR sensor. The 2.0 and 4.0-mm thick test pieces were made by filling a 6.0-mm diameter hole in aluminium rings that were either 2.0 or 4.0-mm thick with RBC. The 0.2-mm thick test pieces were made in a 6-mm diameter hole in a 0.2-mm thick polyester strip. A 50-µm thick polyester (Mylar) sheet was placed on top of the uncured material, which was then pressed into place over the ATR crystal by hand using a flat glass slab. This process forced the uncured composite to conform to the confines of the mold and adapt to both the bottom surface, where the diamond sensing element was located, and to the top surface, where excess RBC was allowed to escape. Two minutes were allowed for the above placement and adaptation steps. By then, the RBC over the heated ATR sensor had reached 32 °C (confirmed separately using thermocouples). The LCU was attached to a mechanical arm that enabled the LCU tip to be reproducibly positioned perpendicularly over the RBC and in contact with the polyester strip over the RBC (Fig. 3)-.

The time delay before polymerization started was determined according to the procedure illustrated in Fig. 4. The time delay was estimated by extrapolating the tangent to the point of maximum rate of change of DC to the 0 % DC (*i.e.* uncured) baseline. The peak conversion rate was calculated after the DC rate was smoothed using a first-order Savitzky-Golay filter with an averaging window of 0.3 s [44].

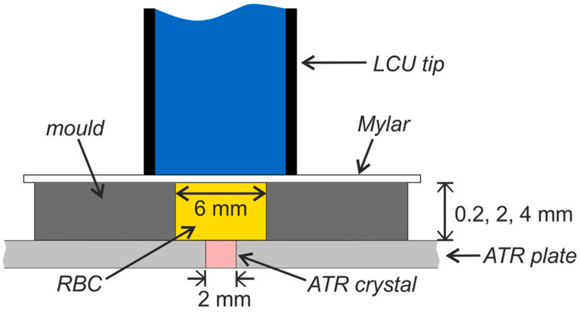

**Fig. 3.** Schematic showing RBC contained in a metal ring mold (2 or 4- mm thick) or a hole in a polyester sheet (0.2 mm) over the ATR crystal. The LCU tip was in contact with the Mylar strip.

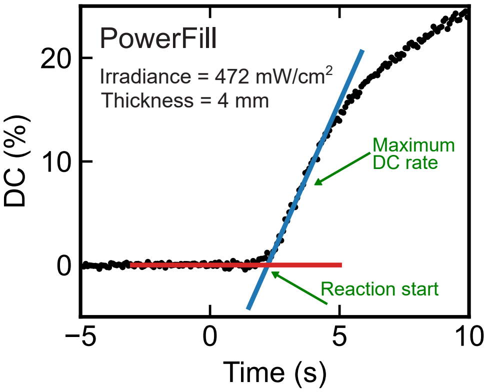

**Fig. 4.** Representative data (black dots) showing the procedure used to estimate the start of polymerization. The time delay was estimated by extrapolating the tangent to the point of maximum rate of change of DC to the 0 % DC (*i.e.* uncured) baseline.

### 2.5. Statistics

A three-way analysis of variance of delay time on irradiance × thickness × RBC was performed using StatView for Windows v. 5.0 (SAS Institute, Cary, NC, USA). The significance probability (*P*) was calculated separately using Mathematica v. 12.2 (Wolfram Research, Champaign, IL, USA).

## 3. Results

Fig. 5a–c illustrate the degree of conversion as a function of time on a logarithmic scale for the six RBCs at the various irradiances and thicknesses. All six RBCs exhibited similar responses to changes in thickness or irradiance.

The time delay before the nominal onset of polymerization for each RBC and condition is shown in Table 3. For Tetric PowerFlow, Tetric PowerFill, and Admira Fusion x-tra, provided that at least 942 mW/cm$^2$ was delivered to the surface, the minimum time delay before polymerization started at the bottom of the 0.2 mm-thick test pieces (representing the top surface) was less than 0.077 s (*i.e.,* less than the time for a single forward-and-back scan of the FT-IR). At the lowest irradiance, 472 mW/cm$^2$, the 4 mm-thick test pieces took as long as ~16 s for the start of polymerization to be detected at the bottom of Neo Spectra. The shortest delay, at 472 mW/cm$^2$, was observed in PowerFlow (~0.60 s). The effects of irradiance and thickness were systematic: increasing irradiance consistently reduced the delay, and increasing thickness always increased it. The nature of this systematic variation is being investigated and will be reported separately.

Table 4 shows the results of the analysis of variance. It is apparent that both irradiance and thickness affect the delay in a highly-significant fashion and that the materials differ significantly. The fact that all interactions are also highly significant means that the main treatment effects (irradiance and thickness) are not simply additive and that they vary between products.

## 4. Discussion

Table 3 and Fig. 5a, b and c show that, where the time-resolution of the system permitted, there was always a delay before conversion was first detectable (*i.e* the onset of polymerization) at the bottom of all six RBCs. This delay decreased systematically with an increase in irradiance

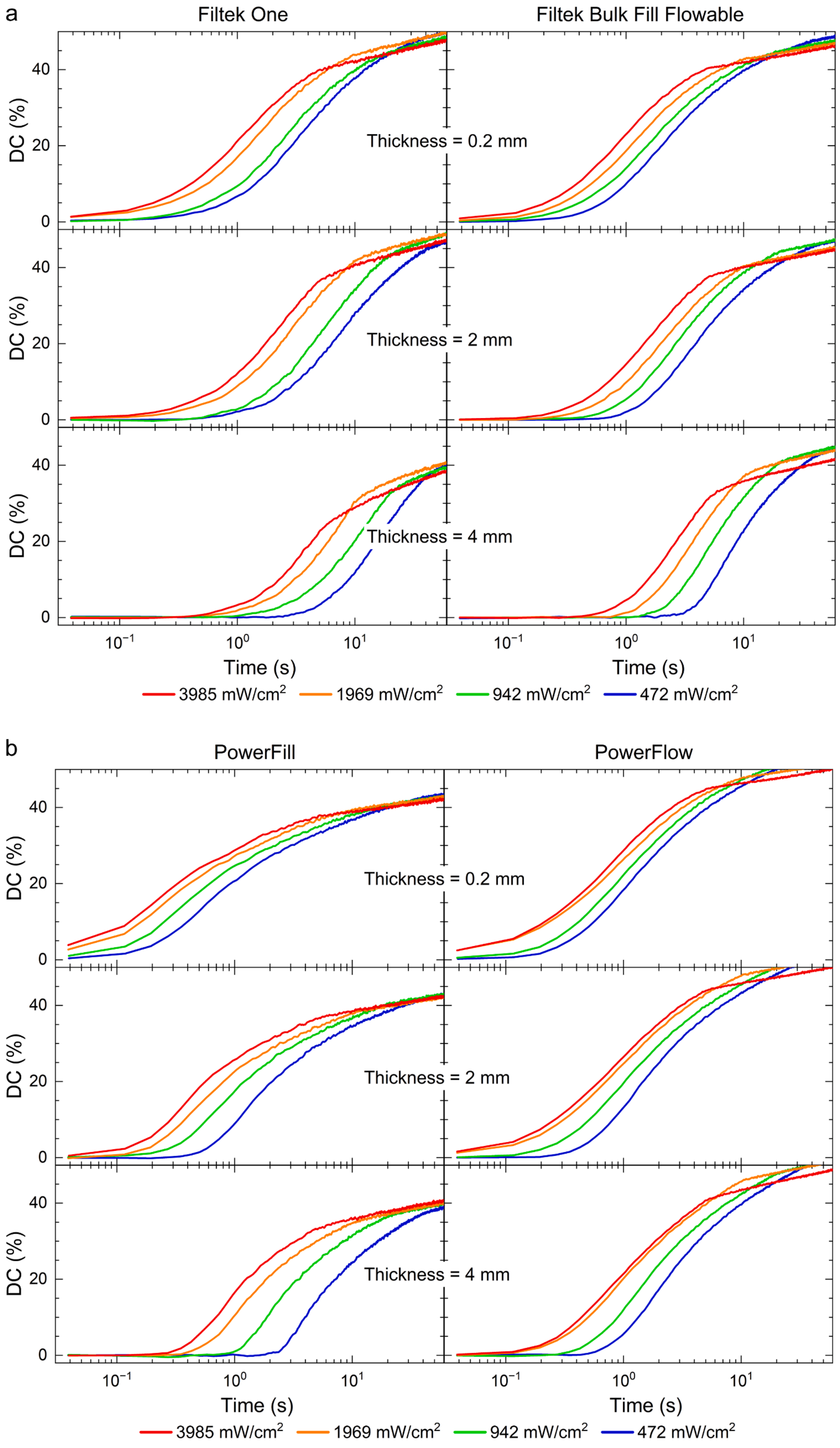

**Fig. 5.** Representative results illustrating the changes in the DC at the bottom surface of the 6 RBCs tested during the first 60 s after the LCU was turned on, 5a: Filtek One, Filtek Bulk-Fill Flowable. 5b: Tetric PowerFill, Tetric PowerFlow, 5c: Admira Fusion x-tra, Neo Spectra ST-LV.

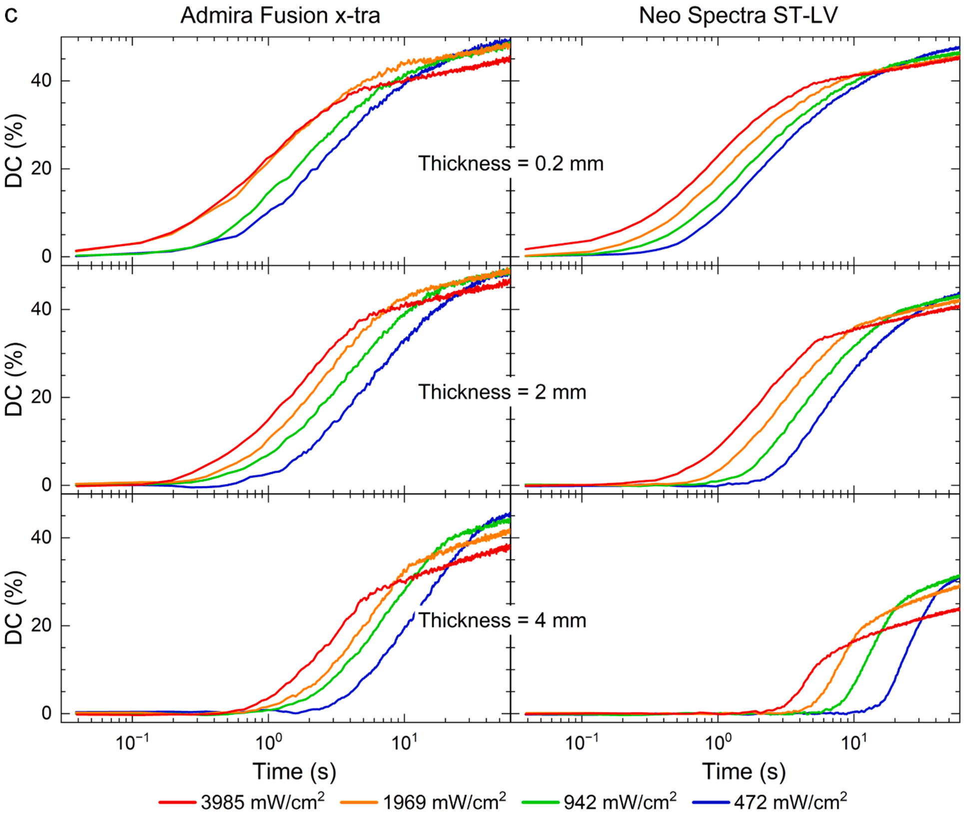

**Fig. 5.** (*continued*).

and a decrease in thickness. This was in accordance with theoretical expectations. Furthermore, the significant variation in delay values under each condition across the six RBCs (Tables 3 and 4), as well as the presence of significant interactions (Table 4), indicate that there are substantial differences between the six products. Thus, all three study goals were met.

The delay before polymerization starts occurs because the inhibitors present must be consumed first. Any free radicals that are first produced, whether primary initiating radicals or propagating radicals on growing polymer chains, are preferentially consumed by these highly-reactive competitors. The consumption rate of these inhibitors depends on the local irradiance within the RBC, which decreases exponentially from its surface [1,2,28–30]. Thus, the reaction rate should decrease with depth, and the time lag depicted in Fig. 1 before polymerization begins must be longer [45]. That is, it takes more time to produce enough 'sacrificial' radicals to react with and cause a fall in the concentration of both inhibitor and the dissolved oxygen to values at which radical addition to monomer, and thus chain propagation, become dominant. This time delay may be somewhat modified by the photobleaching effect [1,2] that occurs as the camphorquinone initiator reacts: less blue light is absorbed, thus allowing more light to be transmitted deeper into the RBC.

Although the occurrence of such a time delay has been reported previously [41,42], this is the first systematic investigation into the effects of thickness and irradiance on that delay. Although the 0.2-mm test pieces were intended to represent the top surface of the material, it is clear that, even at 0.2 mm, a measurable delay still exists, and it cannot be ignored in research on the polymerization kinetics of dental RBCs. As far as the authors are aware, no RBC manufacturer endorses using a 1-s exposure in the instructions for use for any of their RBCs. This would mean that the LCU would have to deliver an irradiance of 20, 000 mW/cm$^2$ to deliver 20 J/cm$^2$ in 1 s.

The 2- and 4-mm test pieces were chosen to represent clinically-relevant thicknesses. To illustrate the problem arising from the delay, a conventional paste-consistency RBC (Neo Spectra), which is intended to be used in increments of at most 2 mm thick (Table 1), was included because clinicians find it difficult to judge the thickness of an intended 2-mm increment in a cavity [46]. At 2 mm and 942 mW/cm$^2$, for Neo Spectra, the delay at the bottom is greater than 1 s (Table 3). This exceeds the minimum 20-s exposure time by more than 5 %. If the thickness were to be greater or the irradiance less, both of which are appreciable clinical risks, Table 3 and Fig. 5a-c illustrate how the problem will be exacerbated. For example, suppose that a clinician believed that a high-power LCU (*e.g.*, 3985 mW/cm$^2$) could photo-cure 4 mm of Neo Spectra (2.69 s delay), Filtek Flowable (0.56 s delay), or Filtek One (0.64 s delay) in 3 s, then the exposure deficit would be increased to ~90 %, 19 % or 21 % of the 3 s exposure, respectively.

There are substantial differences between these six commercial products (Tables 3 and 4; Fig. 5a-c). This observation is not unreasonable because differences in the inhibitor concentrations (if not their chemistry and thus their efficacy) might be expected between manufacturers. Only PowerFill and PowerFlow are designed to be photocured in 3 s, and Table 3 shows that these two RBCs had the least time delay. Differences also arise because there is a steady consumption of inhibitors over time due to background reactions, given that the time between the manufacture date and use varies randomly between products. There are also variations in the scale of the effect that are caused by the thickness of the RBC. This can be attributed to the differences in the rate of light attenuation with depth according to shade and filler content, as well as more complicated behaviour concerning the refractive index. Changes in matrix refractive index due to polymerization and varying temperature will affect the scattering of the light and thus the effective irradiance at the bottom surface.

The clinical relevance of this study lies in the fact that most researchers have not yet considered the delay in polymerization initiation. Even at the highest incident irradiance, there will still be some time after the start of photocuring before the RBC could be bonded to the floor of the filling (Figs. 1 and 5, and Table 3) – up to 0.65 s for the bulk-fill RBCs

**Table 3**
Effect of thickness and irradiance on the mean ± (standard deviation) time delay (in seconds) before polymerization initiation at the bottom surface of the 6 RBCs tested (*values less than the data collection time of 0.077 s).

| **Filtek Flowable Bulk Fill** | | **Irradiance / mW/cm$^2$** | | | |
|---|---|---|---|---|---|
| | | **472** | **942** | **1969** | **3985** |
| **Thickness / mm** | **0.2** | 0.21 ± 0.02 | 0.11 ± 0.01 | 0.03 ± 0.02* | 0.02 ± 0.02* |
| | **2** | 0.73 ± 0.06 | 0.44 ± 0.04 | 0.22 ± 0.02 | 0.15 ± 0.02 |
| | **4** | 2.97 ± 0.06 | 1.67 ± 0.06 | 0.89 ± 0.09 | 0.56 ± 0.07 |
| **Tetric PowerFlow** | | **Irradiance / mW/cm$^2$** | | | |
| | | **472** | **942** | **1969** | **3985** |
| **Thickness / mm** | **0.2** | 0.13 ± 0.01 | 0.07 ± 0.0* | 0 ± 0* | 0 ± 0* |
| | **2** | 0.30 ± 0.01 | 0.12 ± 0.01 | 0.02 ± 0.02* | 0 ± 0* |
| | **4** | 0.60 ± 0.04 | 0.32 ± 0.01 | 0.12 ± 0.01 | 0.09 ± 0.01 |
| **Filtek One Bulk Fill** | | **Irradiance / mW/cm$^2$** | | | |
| | | **472** | **942** | **1969** | **3985** |
| **Thickness / mm** | **0.2** | 0.23 ± 0.02 | 0.10 ± 0.02 | 0.04 ± 0.03* | 0.01 ± 0.01* |
| | **2** | 0.70 ± 0.09 | 0.36 ± 0.10 | 0.18 ± 0.05 | 0.10 ± 0.02 |
| | **4** | 2.78 ± 0.47 | 1.63 ± 0.07 | 0.91 ± 0.08 | 0.64 ± 0.08 |
| **Tetric PowerFill** | | **Irradiance / mW/cm$^2$** | | | |
| | | **472** | **942** | **1969** | **3985** |
| **Thickness / mm** | **0.2** | 0.10 ± 0.02 | 0.04 ± 0.03* | 0.01 ± 0.01* | 0 ± 0* |
| | **2** | 0.46 ± 0.02 | 0.22 ± 0.02 | 0.11 ± 0.01 | 0.05 ± 0.03* |
| | **4** | 2.12 ± 0.04 | 0.96 ± 0.05 | 0.45 ± 0.08 | 0.30 ± 0.01 |
| **Admira Fusion x-tra** | | **Irradiance / mW/cm$^2$** | | | |
| | | **472** | **942** | **1969** | **3985** |
| **Thickness / mm** | **0.2** | 0.06 ± 0.02* | 0.07 ± 0.05* | 0 ± 0* | 0 ± 0* |
| | **2** | 0.59 ± 0.08 | 0.23 ± 0.05 | 0.16 ± 0.03 | 0.06 ± 0.03* |
| | **4** | 2.27 ± 0.33 | 1.30 ± 0.42 | 0.95 ± 0.03 | 0.65 ± 0.04 |
| **TPH Neo Spectra** | | **Irradiance / mW/cm$^2$** | | | |
| | | **472** | **942** | **1969** | **3985** |
| **Thickness / mm** | **0.2** | 0.24 ± 0.02 | 0.13 ± 0.02 | 0.06 ± 0.02* | 0.01 ± 0.01* |
| | **2** | 2.08 ± 0.07 | 1.11 ± 0.03 | 0.56 ± 0.05 | 0.33 ± 0.01 |
| | **4** | 15.91 ± 1.04 | 7.79 ± 0.25 | 5.17 ± 0.49 | 2.69 ± 0.20 |

**Table 4**
Analysis of variance of irradiance × thickness × RBC.
DF: degrees of freedom; *P*: significance probability.

| | DF | Sum of Squares | Mean Square | *F*-ratio | *P* |
|---|---|---|---|---|---|
| **Irradiance** | 3 | 69.451 | 23.150 | 551.531 | $1 \times 10^{-78}$ |
| **Thickness** | 2 | 197.876 | 98.938 | 2357.083 | $1 \times 10^{-111}$ |
| **RBC** | 5 | 198.222 | 39.644 | 944.481 | $4 \times 10^{-108}$ |
| **Irradiance × Thickness** | 6 | 71.706 | 11.951 | 284.717 | $3 \times 10^{-77}$ |
| **Irradiance × RBC** | 15 | 79.699 | 5.313 | 126.582 | $6 \times 10^{-75}$ |
| **Thickness × RBC** | 10 | 280.345 | 28.034 | 667.889 | $3 \times 10^{-115}$ |
| **Irradiance × Thickness × RBC** | 30 | 112.981 | 3.766 | 89.721 | $1 \times 10^{-78}$ |
| **Residual** | 144 | 6.044 | 0.042 | | |

and 2.69 s for Neo Spectra. Thus, the bottom surface of the RBC will not be bonded to the tooth until after the top surface hardens. While this problem could be minimized by photocuring a thin layer of RBC first, the current trend is for bulk filling and bulk curing. This delay between when polymerization starts at the pulpal floor compared with the top of the filling may be responsible for the shrinkage gaps produced at the pulpal floor of a restoration that have been observed using optical coherence tomography (OCT) and X-ray micro-computed tomography (μ-CT) [47–49]. Clinically, this means that even though bulk-fill RBCs might be adequately photocured in 4-mm increments, the first increment should be thin. However, because the current trend is toward bulk filling and bulk curing, manufacturers could attempt to initiate polymerization at the interface between the bonding agent and the RBC. This has already been accomplished in one RBC using its matched priming agent [50].

This study has enhanced the understanding of how light exposure conditions influence the occurrence of a polymerization delay at the bottom of six RBCs. The results show that nearly all previous conclusions regarding the reaction kinetics of RBCs should be re-evaluated, as these findings were based on treating the polymerization reaction as starting instantaneously upon light exposure [15,20,31–35,37,39]. Unfortunately, the spectral data reported in those studies were not collected at a high enough rate to determine when polymerization effectively started, and the curve fitting of the data – using various techniques – failed to account for the possibility of a delay at the bottom of the RBC before polymerization started. Although the effects of this delay may not impact the final DC if a sufficiently long exposure is used, appreciating that there is a measurable delay before polymerization starts at the bottom surface is crucial now that some LCU manufacturers claim their devices can adequately photocure RBCs in 1 s [10–12]. While most dentists desire a high-irradiance short-duration exposure [9], dentists should now understand that as much as ~60 % of a 1 s exposure (0.56–0.65 s) may be spent consuming the inhibitors at the bottom of a 4-mm increment, as seen for example in Admira Fusion x-tra, Filtek One, and Filtek BulkFill Flow (Table 3). This finding may explain the poor results reported when a diode laser was used for 1 s compared with a 10- or 20-s exposure time using conventional LED curing lights [20–24].

The existence of a delay before the effective initiation of polymerization at the bottom of any thickness of RBC has important implications for:

- the instrument requirements for studying the development of the DC in terms of temporal resolution and signal-to-noise ratio;
- the analytical or curve-fitting models used for studying the kinetics of such systems, *i.e.* those models must include the inhibitor-based delay;
- the clinical procedure to be used to ensure adequate polymerization at the bottom of any increment and thus effective treatment;
- the need to recognize that manufacturers' instructions are made under idealized conditions;
- that recommended light curing conditions should be based on the behaviour at the bottom of the increment;

### *4.1. Limitations*

Fig. 5 and Table 3 show that when data were collected using the highest irradiance for the smallest thickness (effectively representing the top surface of a filling), the time delay was less than the 0.077 s it took to make the first forward and backward scan. While there is some variation, several conditions had this result, marked by the asterisks in Table 3. This illustrates the effects of the precision of the equipment, RBC composition, and the effect of the attenuation of light as the thickness of the RBC increased [28–30]. The FT-IR time resolution of 0.077 s was insufficient to estimate when polymerization effectively started for some high irradiances at the 0.2-mm thickness, or even at 2 mm in some RBCs (Table 3, asterisks). Ideally, faster equipment should be used in future studies of polymerization kinetics.

## 5. Conclusions

The confirmation of a delay in the onset of polymerization indicates that:

1. Future studies of photocuring kinetics should be reported under conditions that allow adequate time-resolution using models that include an "offset" parameter to account for the time delay before polymerization starts at the bottom surface;
2. Some RBCs have a longer delay; and
3. The instructions for use should be modified to account for and the effects of thickness and irradiance on this delay.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Raw data is available upon reasonable request by contacting the corresponding author.

## References

[1] Hadis MA, Shortall AC, Palin WM. The power of light - From dental materials processing to diagnostics and therapeutics. Biomater Invest Dent 2024;11:40308. https://doi.org/10.2340/biid.v11.40308.

[2] Watts DC. Light-curing dental resin-based composites: how it works and how you can make it work. Front Dent Med 2023;4:1108316. https://doi.org/10.3389/fdmed.2023.1108316.

[3] Neo Spectra Instructions for use. Dentsply Sirona. Konstanz, Germany. 2018.

[4] TetricPowerFill: Instructions for Use. Ivoclar Vivadent AG, Schaan, Liechtenstein. 2018.

[5] TetricPowerFlow: Instructions for Use. Ivoclar Vivadent AG, Schaan, Liechtenstein. 2018.

[6] Admira Fusion x-tra Instructions for Use VOCO Cuxhaven, Germany.

[7] Filtek Bulk Fill Flowable Restorative: Instructions for Use. 3M Oral Care, St. Paul, MN, USA. 2014.

[8] Filtek One Bulk Fill Restorative: Instructions for Use. 3M OralCare. St. Paul, MN, USA. 2016.

[9] Frazier K, Bedran-Russo AK, Lawson NC, Park J, Khajotia S, Urquhart O. Dental light-curing units: An American Dental Association Clinical Evaluators Panel survey. J Am Dent Assoc 2020;151(544–5):e2–545. https://doi.org/10.1016/j.adaj.2020.03.001.

[10] 3s PowerCure. Scientific Documentation. Schaan, Liechtenstein: Ivoclar Vivadent; 2019.

[11] FlashMax P3 Product description. CMS Dental. Roslev, Denmark. 2021.

[12] Monet Laser Curing Light. The 1 second revolution. AMD. West Jordan, UT, USA. 2021.

[13] Leprince JG, Hadis M, Shortall AC, Ferracane JL, Devaux J, Leloup G, Palin WM. Photoinitiator type and applicability of exposure reciprocity law in filled and unfilled photoactive resins. Dent Mater 2011;27:157–64. https://doi.org/10.1016/j.dental.2010.09.011.

[14] Hadis M, Leprince JG, Shortall AC, Devaux J, Leloup G, Palin WM. High irradiance curing and anomalies of exposure reciprocity law in resin-based materials. J Dent 2011;39:549–57. https://doi.org/10.1016/j.jdent.2011.05.007.

[15] Negovetic Mandic V, Par M, Marovic D, Rakic M, Tarle Z, Klaric Sever E. Blue laser for polymerization of bulk-fill composites: influence on polymerization kinetics. Nanomaterials 2023;13:13. https://doi.org/10.3390/nano13020303.

[16] Lempel E, Szebeni D, Őri Z, Kiss T, Szalma J, Lovász BV, Kunsági-Máté S, Böddi K. The effect of high-irradiance rapid polymerization on degree of conversion, monomer elution, polymerization shrinkage and porosity of bulk-fill resin composites. Dent Mater 2023;39:442–53. https://doi.org/10.1016/j.dental.2023.03.016.

[17] Tichy A, Bradna P. Applicability of exposure reciprocity law for fast polymerization of restorative composites containing various photoinitiating systems. Oper Dent 2021;46:406–18. https://doi.org/10.2341/20-112-L.

[18] Sadeghyar A, Watts DC, Schedle A. Limited reciprocity in curing efficiency of bulk-fill resin-composites. Dent Mater 2020;36:997–1008. https://doi.org/10.1016/j.dental.2020.04.019.

[19] Selig D, Haenel T, Hausnerová B, Moeginger B, Labrie D, Sullivan B, Price RB. Examining exposure reciprocity in a resin based composite using high irradiance levels and real-time degree of conversion values. Dent Mater 2015;31:583–93. https://doi.org/10.1016/j.dental.2015.02.010.

[20] Thanoon H, Price RB, Watts DC. Thermography and conversion of fast-cure composite photocured with quad-wave and laser curing lights compared to a conventional curing light. Dent Mater 2024;40:546–56. https://doi.org/10.1016/j.dental.2024.01.003.

[21] Maucoski C, Price RB, Rocha MG, Roulet JF, Sullivan B. Ability of short exposures from laser and quad-wave curing lights to photo-cure bulk-fill resin-based composites. Dent Mater 2023;39:275–92. https://doi.org/10.1016/j.dental.2023.01.007.

[22] Rocha MG, Maucoski C, Roulet JF, Price RB. Depth of cure of 10 resin-based composites light-activated using a laser diode, multi-peak, and single-peak light-emitting diode curing lights. J Dent 2022;122:104141. https://doi.org/10.1016/j.jdent.2022.104141.

[23] Comisi JC, Maucoski C, Beller JP, Dennis KS, Price RB. A blinded comparative study of four commercially available LEDs and a laser light curing device. Eur J Dent 2023;17:1065–74. https://doi.org/10.1055/s-0042-1757908.

[24] Comisi JC, Price RB, Kinley-Howard K, Maucoski C, Rader E. Ability of six curing lights to photocure four resin-based composites in a MOD-mold: a double-blind study. Eur J Prosthodont Restor Dent 2024;32:301–13. https://doi.org/10.1922/EJPRD_2661Comisi13.

[25] Howard B, Wilson ND, Newman SM, Pfeifer CS, Stansbury JW. Relationships between conversion, temperature and optical properties during composite photopolymerization. Acta Biomater 2010;6:2053–9. https://doi.org/10.1016/j.actbio.2009.11.006.

[26] Filtek Bulk Fill Restorative Technical Product Profile. 3 M OralCare. St. Paul, MN, USA. 2016.

[27] Darvell BW. Materials Science for Dentistry. tenth ed. Duxford, United Kingdom: Woodhead Publishing; 2018.

[28] Harlow JE, Rueggeberg FA, Labrie D, Sullivan B, Price RB. Transmission of violet and blue light through conventional (layered) and bulk cured resin-based composites. J Dent 2016;53:44–50. https://doi.org/10.1016/j.jdent.2016.06.007.

[29] Ilie N. The dependence on hue, value and opacity of real-time- and post-curing light transmission in a nano-hybrid ormocer. Materials 2024;17:17. https://doi.org/10.3390/ma17020496.

[30] Ilie N, Furtos G. A comparative study of light transmission by various dental restorative materials and the tooth structure. Oper Dent 2020;45:442–52. https://doi.org/10.2341/19-037-L.

[31] Ilie N. Comparative effect of self- or dual-curing on polymerization kinetics and mechanical properties in a novel, dental-resin-based composite with alkaline filler. Materials 2018;11:11. https://doi.org/10.3390/ma11010108.

[32] Ilie N, Watts DC. Outcomes of ultra-fast (3 s) photo-cure in a RAFT-modified resin-composite. Dent Mater 2020;36:570–9. https://doi.org/10.1016/j.dental.2020.02.007.

[33] Burrer P, Par M, Fürer L, Stübi M, Marovic D, Tarle Z, Attin T, Tauböck TT. Effect of polymerization mode on shrinkage kinetics and degree of conversion of dual-curing bulk-fill resin composites. Clin Oral Invest 2023;27:3169–80. https://doi.org/10.1007/s00784-023-04928-0.

[34] Seoane H, Chasqueira F, Azul AM, Polido M, Delgado AH. Impact of shelf-life simulation on a self-adhesive composite: polymerization kinetics, chemical and color stability. J Adhes Dent 2023;25:167–76. https://doi.org/10.3290/j.jad.b4368821.

[35] Marovic D, Haugen HJ, Par M, Linskens S, Mensikova E, Negovetic Mandic V, Leeuwenburgh S, Nogueira LP, Vallittu PK, Ma Q. Emerging technologies for the evaluation of spatio-temporal polymerisation changes in flowable vs. sculptable dental resin-based composites. Dent Mater 2024;40:1895–908. https://doi.org/10.1016/j.dental.2024.09.002.

[36] Strazzi-Sahyon HB, Hadis MA, Dos Santos PH, Palin WM. The effect of photoinitiator type and filler load on physicochemical and mechanical properties of experimental light-cured resin cements through lithium disilicate ceramics of different shades and thicknesses. Dent Mater 2024;40:1452–63. https://doi.org/10.1016/j.dental.2024.06.020.

[37] Algamaiah H, Alshabib A, Algomaiah M, Yang J, Watts DC. Diversity of short-term DC outcomes in bulk-fill RBCs subjected to a 3 s high-irradiance protocol. Dent Mater 2024;40:1872–80. https://doi.org/10.1016/j.dental.2024.08.008.

[38] Wang K, Peng Q, Yao J, Wang Z. Accurate assessment of the three-dimensional shrinkage stress evolution for photopolymerized dental filling materials: mechano-chemo-thermo-coupled finite element modeling and experimental validation. Dent Mater 2025;41:319–30. https://doi.org/10.1016/j.dental.2024.12.005.

[39] Alayed A, Silikas N, Watts DC. The effect of photoinitiator systems on resin-based composite containing ZnO-nanoparticles. Dent Mater 2025;41:220–8. https://doi.org/10.1016/j.dental.2024.12.002.

[40] Yoshihara K, Nagaoka N, Benino Y, Nakamura A, Hara T, Maruo Y, Yoshida Y, Van Meerbeek B. Touch-cure polymerization at the composite cement-dentin interface. J Dent Res 2021;100:935–42. https://doi.org/10.1177/00220345211001020.

[41] Labrie D, Price RB, Sullivan B, Salazar AM, Gautam D, Stansbury JW, Ferracane JL. Effect of thickness on the degree of conversion of two bulk-fill and one conventional posterior resin-based composites at high irradiance and high temporal resolution. J Mech Behav Biomed Mater 2022;136:105489. https://doi.org/10.1016/j.jmbbm.2022.105489.

[42] Sullivan B, Kalliecharan D, Kostylev I, Earle G, Stansbury JW, Price RB, Labrie D. Photo-polymerization kinetics of a dental resin at a high temporal resolution. J Mech Behav Biomed Mater 2021;124:104884. https://doi.org/10.1016/j.jmbbm.2021.104884.

[43] Rueggeberg FA, Daronch M, Browning WD, DEG MF. In vivo temperature measurement: tooth preparation and restoration with preheated resin composite. J Esthet Restor Dent 2010;22:314–22. https://doi.org/10.1111/j.1708-8240.2010.00358.x.

[44] Savitzky A, Golay MJE. Smoothing and differentiation of data by simplified least squares procedures. Anal Chem 2002;36:1627–39. https://doi.org/10.1021/ac60214a047.

[45] Musanje L, Darvell BW. Curing-light attenuation in filled-resin restorative materials. Dent Mater 2006;22:804–17. https://doi.org/10.1016/j.dental.2005.11.009.

[46] Sword RJ, Bachand W, Mears B, Quibeuf L, Looney S, Price RB, Rueggeberg FA. Effect of operator experience on ability to place sequential, 2-mm-thick increments of composite. Oper Dent 2021;46:327–38. https://doi.org/10.2341/19-286-L.

[47] Hayashi J, Tagami J, Chan D, Sadr A. New bulk-fill composite system with high irradiance light polymerization: integrity and degree of conversion. Dent Mater 2020;36:1615–23. https://doi.org/10.1016/j.dental.2020.10.012.

[48] Bakhsh TA, Tagami J, Sadr A, Luong MN, Turkistani A, Almhimeed Y, Alshouibi E. Effect of light irradiation condition on gap formation under polymeric dental restoration; OCT study. Z Med Phys 2020;30:194–200. https://doi.org/10.1016/j.zemedi.2020.02.001.

[49] Kweon HJ, Ferracane J, Kang K, Dhont J, Lee IB. Spatio-temporal analysis of shrinkage vectors during photo-polymerization of composite. Dent Mater 2013;29:1236–43. https://doi.org/10.1016/j.dental.2013.09.011.

[50] Guarneri JAG, Maucoski C, Ghaffari S, MacNeil BD, Price RB, Arrais CAG. Ability of a novel primer to enhance the polymerization of a self-cured resin composite. Dent Mater 2025;41:42–50. https://doi.org/10.1016/j.dental.2024.10.013.