Effects of extended curing time on the diametral tensile strength, degree of conversion, and monomer release of bulk-fill composite resins

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Effects of extended curing time on the diametral tensile strength, degree of conversion, and monomer release of bulk-fill composite resins

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Abstract. This study aims to evaluate the effects of extended curing of bulk-fill composite resins with a light-emitting diode (LED) by investigating the diametral tensile strength (DTS), degree of conversion (%DC), and bis-GMA monomer release (MR). A total of 144 specimens (diameter, 5 mm and thickness, 4 mm) with three different bulk-fill composite resins were investigated by divided them into three groups with curing times of 20, 25, and 30 s, with LED irradiance of 900 mW/cm\textsuperscript{2}. After 24 h of curing, each specimen was analyzed using a universal testing machine, Fourier-transform infrared (FTIR) spectroscopy, and high-performance liquid chromatography (HPLC) to determine the DTS, %DC, and bis-GMA MR, respectively. The data were analyzed using a one-way ANOVA (\( \alpha = 0.05 \)). It was observed that DTS increased as the curing time increased for all resins tested but only the differences in the FBF samples were statistically significant. The %DC was in the range 45.92\% – 74.65\% but was not affected by curing time (\( P \geq 0.05 \)). FBF exhibited the lowest MR of all the resins. It can be concluded that extending the LED curing time increases the DTS of bulk-fill composite resins but did not affect the %DC or MR.

1. Introduction
Light-activated composite resins are the most commonly used materials in modern restorative dentistry [1,2]. However, due to the limited depth of cure with the conventional light-activation process, the composite resin must be applied with a maximum depth of 2 mm to ensure adequate light transmission and sufficient polymerization [1,3]. Thus, in cavities deeper than 2 mm, layers of the composite resin must be applied incrementally, which can be a time-consuming process. Newly developed bulk-fill composite resins have been reported to have a depth of cure up to 4 mm so they can be applied in a single bulk application and, thus, save time when filling larger cavities [1,3].

In general, a large depth of cure can be achieved if the resin has a high degree of conversion (%DC) [4], which is defined as the percentage of carbon-carbon double bonds that were converted into single bonds to form the polymeric resin [4,5]. It is expected that composite resins with large depths of cure will have better mechanical properties such as diametral tensile strength [5]. However, resin monomers
can be released if the polymerization process is inadequate, irritating the soft tissue (such as the mucosa and pulp), stimulate bacterial growth, and inducing allergic and cytotoxic reactions [6]. Bisphenol-A-glycerolate dimethacrylate (bis-GMA) is one of the most commonly used monomers in composite resin and it acts as a matrix in the resin. However, it contains bisphenol A (BPA) derivatives, known as estrogenic compounds; BPA is suspected to have negative effects on fetal and infant brain development and behavior [4,5,7]. The United States Environmental Protection Agency (EPA) defines the maximum safe dose of BPA to be 50 μg/kg body-weight/day but the animal studies have indicated that exposure to even low doses (0.025–2.5 μg/kg body-weight/day) could have long-term adverse effects on the reproductive system and can have carcinogenic effects [7].

The curing time of the light-curing unit is known to affect the %DC [4,5]. The manufacturer's instructions for some commercial composite resin products suggest that curing be done for 20 s using a light-emitting diode (LED) with an irradiance of less than 1000 mW/cm² [8]. Previous studies have reported that extending this curing time increases the %DC and the microhardness [9]. Therefore, the purpose of this study was to evaluate the effects of extended LED curing time on the diametral tensile strength (DTS), %DC, and bis-GMA monomer release (MR) of three different bulk-fill composite resins.

2. Methods

2.1. Materials
Three commercially available bulk-fill composite resins, Giomer Beautifil-Bulk Restorative® Bulk Fill (GBF, Shofu, Japan), Tetric N-Ceram® Bulk Fill (TBF, Ivoclar-Vivadent, Liechtenstein), and Filtek™ Bulk Fill (FBF, 3M-ESPE, Germany) as listed in Table 1 were investigated. Bisphenol-A-glycerolate dimethacrylate (bis-GMA, C_{29}H_{36}O_8, 512.59 g/mol molecular weight, CAS Number 1565-94-2, Sigma Aldrich) as listed in Table 2 was used as the monomer.

| Bulk-fill Composite Resins | Monomer/resin matrix | Fillers | Filler (wt.%) | Manufacturer |
|---------------------------|----------------------|---------|--------------|--------------|
| Giomer Beautifil-Bulk Restorative® (GBF) | Bis-GMA, UDMA, Bis-MPEPP, TEGDMA | S-PRG filler based on F–B–Al–Si-glass (0.8 μm) | 87.0 | Shofu, Japan |
| Tetric® N-Ceram Bulk Fill (TBF) | Dimethacrylates monomers | Barium glass filler (0.4–0.7 μm), ytterbium trifluoride (200 nm), mixed oxide (160 nm), and polymer filler | 78.0 | Ivoclar-Vivadent, Liechtenstein, Germany |
| Filtek™ Bulk-Fill (FBF) | AUDMA, Bis-GMA, AFM, DDDMA, UDMA | Agglomerate (100 nm), ytterbium trifluoride, combination of a non-agglomerated/non-aggregated (20 nm) silica, non-agglomerated/non-aggregated (4–11 nm) zirconia, aggregated zirconia/silica clusters (20 nm silica and 4–11 nm zirconia particles) | 76.5 | 3M-ESPE, USA |
Table 2. Standard monomer used for HPLC

| Substances | Monomer        | Chemical type | Molecular weight | CAS-number | Company                          |
|------------|----------------|---------------|-------------------|------------|----------------------------------|
| Bis-GMA    | Bisphenol A glycerolate dimethacrylate | C$_{29}$H$_{36}$O$_8$ | 512.59 g/mol      | 1565-94-2  | (Sigma-Aldrich, USA)             |

2.2. Specimen Preparation
Uncured bulk-fill composite resin was inserted in bulk into a cylindrical mold of 5 mm in diameter and 4 mm in thickness. A transparent mylar strip was placed on the top and bottom of the mold to prevent oxygen from inhibiting the curing. Each specimen was cured for 20, 25, and 30 s with an LED curing unit (900 mW/cm$^2$, Hilux Ledmax 450, Dentaurum, Germany) with the light tip in contact with the mylar strip on the specimen surface. A total of 144 specimens of the three bulk fill composite resins were created.

2.3. Diametral Tensile Strength (DTS)
After light curing, all specimens (n=10) were removed from the mold and stored for 24 h in 1 ml of distilled water at 37°C before testing. DTS was performed using a universal testing machine (Shimadzu AG-5000, Japan) with a 250 kgF load cell.

2.4. Degree of Conversion (%DC)
After light curing, all specimens (n=3) were stored dry for 24 h at 37°C. Then, each sample was analyzed using Fourier-transform infrared (FTIR) spectroscopy (Perkin Elmer, USA) to obtain the %DC. The absorption spectrum for each specimen as well as that for the uncured material were created from 45 scans at a resolution of 4 cm$^{-1}$ over the wavelength range of 450–4000 cm$^{-1}$. The peak heights at 1638 cm$^{-1}$ (aliphatic carbon double bonds) and 1608 cm$^{-1}$ (aromatic carbon double bonds) were measured. The %DC was then calculated as the reduction in the absorbance at 1638 cm$^{-1}$ between the uncured and cured specimens using the following equation:

2.5. Bis-GMA Monomer Release (MR)
All specimens (n=3) were weighed after light curing and were then immersed in 1 ml of a 75 vol% ethanol/water solution in brown glass vials for 24 h at room temperature. Bis-GMA standard solutions were prepared by diluting the monomer in the 75% ethanol/water solution to relevant concentrations (50, 100, 250, and 500 ppm). The MR was analyzed using HPLC (high-performance liquid chromatography, Shimadzu, Japan) with 20 µl of sample in a Phenomenex 100-5C18 250 mm × 4.6 mm column using a mobile phase of 80% CH$_3$CN (acetonitrile) and 20% ultrapure H$_2$O (water) flowed at a rate of 1 ml/min. Detection was performed at a wavelength of 275 nm.$^6$ The linearity of the assay was checked by calculating the regression line using the least squares method; the coefficient of determination was found to be R$^2$ = 0.9999, indicating good linearity in the range of 50–500 ppm. The obtained calibration curve and the equation expressing the linear relation are shown in Figure 1.

2.6. Statistical Analysis
Statistical analysis was performed using SPSS 16.0. One-way ANOVA and post-hoc tests were used to evaluate the DTS and MR results. Kruskal–Wallis test was used to analyze the %DC. A significance level of 0.05 was assumed for the statistical analysis.
3. Results

DTS, %DC, and MR mean and standard deviation values of the materials are presented in Tables 3–5. Table 3 shows that DTS mean value of all materials increased with increasing curing time, but no statistically differences among all groups except for FBF (30 s; 47.90±5.50 MPa). The respective DTS mean values shown in the results were FBF>GBF>TBF. The %DC of all materials at each curing time were not statistically different (P ≥ 0.05) with %DC range of 45.92%–74.65% (Table 4). In MR, FBF showed the lowest bis-GMA MR (20 s: 0.0079 w/v%; 25s: 0.0058 w/v%; 30 s: 0.0067 w/v%) or in the range 67.02–78.55 ppm (µg/ml). There were no statistical differences among all curing time among the same material, but there were statistically significant differences in each curing time between 3 different materials (Table 5).

**Table 3.** Mean and SD of the DTS values (MPa)

| Materials | Curing Time (Mean ± SD) |
|-----------|-------------------------|
|           | 20 s                   | 25 s                   | 30 s                   |
| GBF       | 38.91 ± 3.17           | 40.55 ± 2.77           | 41.22 ± 3.10           |
| TBF       | 35.90 ± 2.78           | 37.47 ± 5.03           | 39.67 ± 3.15           |
| FBF       | 40.13 ± 4.00*          | 45.63 ± 4.46*          | 47.90 ± 5.50*          |

*Significant at P < 0.05 based on a one-way ANOVA and post-hoc tests

**Table 4.** Degree of conversion (%DC) mean and SD values (%)

| Materials | Curing Time (Mean ± SD) |
|-----------|-------------------------|
|           | 20 s                   | 25 s                   | 30 s                   |
| GBF       | 55.15 ± 9.95           | 53.85 ± 11.53          | 53.20 ± 2.52           |
| TBF       | 52.44 ± 12.33          | 74.65 ± 8.53           | 57.89 ± 9.69           |
| FBF       | 45.92 ± 5.72           | 54.00 ± 4.56           | 61.66 ± 5.77           |

Results not statistically significant at a significance level of α = 0.05 using a Kruskal–Wallis test

**Table 5.** Mean and SD of bis-GMA MR values (w/v%)

| Materials | Curing Time (Mean ± SD) |
|-----------|-------------------------|
|           | 20 s                   | 25 s                   | 30 s                   |
| GBF       | 0.0116 ± 0.0032         | 0.0087 ± 0.0010        | 0.0096 ± 0.0016        |
| TBF       | 0.0286 ± 0.0008         | 0.0302 ± 0.0021        | 0.0261 ± 0.0044        |
| FBF       | 0.0079 ± 0.0004*        | 0.0058 ± 0.0007*       | 0.0067± 0.0011*        |

*Significant at P < 0.05 based on a one-way ANOVA and post-hoc tests
4. Discussion

The results show that DTS increased proportionally with greater curing times in all composite resins that were tested in this study. This finding is consistent with the results of a previous study that suggested that extended curing time can improve the hardness (different mechanical property) of bulk-fill composite resins [10]. This may be because the monomers are not adequately polymerized if the curing time is too short, resulting in poor mechanical properties, but longer curing times cause more monomers to polymerize, resulting in a greater mechanical strength and other properties [4]. In the proposed study, the differences in the DTS values of the same materials with different curing times were not statistically significant; although, there was a notable increasing trend in the DTS. However, there were statistically significant differences in the DTS values between different materials. The FBF exhibited the highest DTS values for each exposure time. This could be due to the different composition of FBF. The matrixes of bulk-fill composite resins have been developed to improve the polymerization [11]. Fillers have been developed to improve the mechanical properties of bulk-fill composite resins such as DTS, influence the polymerization, and improve the translucency [4]. Using metal and glass materials in composite resins can also increase the strength [4]. Moreover, increasing the filler loading can improve the mechanical properties; dispersing particles with a range of sizes (e.g., inserting small particles among larger particles) is one way of increasing the filler loading [4].

Table 1 shows that FBF contains ytterbium trifluoride filler agglomerate (YbF3) and a combination of non-agglomerated/non-aggregated silica fillers, non-agglomerated/non-aggregated zirconia, and nanoparticle-aggregated zirconia/silica clusters are introduced with intend to increase the filler loading. The nanocluster particles contained in the FBF are synthesized by sintering and silanization such that they have good mechanical and optical properties [5]. Using a combination of nanomers and nanocluster particles can explain the relatively high DTS values observed for FBF. The DTS values of GFB were higher than those of TBF even though the filler particle size was almost the same size in the two reins. The filler used in GFB is unique as it contains a surface-preracted glass (S-PRG) ionomer as a filler because F-B-Al-Si-glass provides good mechanical properties. PRG fillers are fabricated by an acid–base reaction between fluoroalumino–silicate glass (FASG) and polyalkenoic acid (PAA) in the presence of water to form a wet siliceous hydrogel; the obtained xerogel is then freeze dried, milled, and silanized to form PRG fillers of a specific size range. The reaction was detected in surface-loads and, therefore, was called a surface reaction; thus, the filler is called an S-PRG filler. In a previous study, it was reported that giorner has a higher compressive strength than compomers and other composites without S-PRG [12].

The differences between the %DC values measured at different curing times and in different materials were not statistically significant except in FBF. The %DC of FBF increased as the curing time increased but the difference was not statistically significant, which shows that the curing time did not influence %DC. This contradicts the conclusion of a previous study that reported that the extended curing time with a constant irradiance may increase the %DC [13]. However, another study reported that very short curing times may also result in a higher %DC in bulk-fill composite resins depending on the photoinitiator used in the resin [14]. The matrix monomers can also influence the %DC. This previous study also showed that the %DC was also influenced by the composition of the composite resin. Bis-GMA, as the main monomer in the composite resin matrix, has a very high viscosity so it needs to be diluted in a monomer, such as TEGDMA (triethyleneglycol dimethacrylate) or UDMA (urethane dimethacrylate), to reduce the viscosity of the resin [4,5]. It was shown that bulk-fill composite resins containing UDMA and TEGDMA without bis-GMA have higher %DC values, [15] It has also been reported that the bulk-fill composite resins containing UDMA, which has a lower viscosity than bis-GMA, in the resin matrix have the best %DC values [3]. All materials used in this present study contain UDMA monomers, which may explain why the %DC values of these materials were not significantly different despite the increasing curing time.

The bis-GMA MR did not change significantly with the curing time within the same material. However, there were statistically significant differences between different materials with the same curing time. FBF exhibited the lowest bis-GMA MR. This is likely because each material has a different monomer matrix composition. All materials contain UDMA monomers, which can increase the DC %, but FBF also has other monomers such as AUDMA (aromatic urethane dimethacrylate), DDDMA (dodecanediol dimethacrylate), and AFM (addition-fragmentation monomers). The stiffness
of the polymer matrix due to the presence of bis-GMA can be decreased by the addition of UDMA and AUDMA monomers [11]. DDDMA monomers have a hydrophobic backbone that allows for further movement of the molecules, improves the material’s compatibility with nonpolar resins [11], and decrease both the viscosity and volatility of the resin. AFM monomers contain a third reactive site that is cleaved through a fragmentation process during polymerization [11]. This process provides a mechanism for the relaxation of the developing network and subsequent stress relief. The fragments, however, still retain the ability to react with each other or other reactive sites of the developing polymer. The combination of these monomers in FBF both reduces the stiffness caused by the presence of bis-GMA and increases the polymerization [11]. As a result, the residual bis-GMA was found to be eluted in small quantities in the immersion solution (about 67.02–78.55 ppm (µg/ml)). The concentration is far lower than the maximum safe dose of BPA specified by the United States EPA [7].

Among all the materials investigated in this study, FBF showed many advantages when used as a restorative material owing to its high DTS that overcomes its brittleness. It has adequate polymerization and small amount of MR which is still safe for health. However, the composition of bulk-fill composite resins also affects its mechanical properties, %DC, and MR. Clinicians are expected to know the composition of bulk-fill composite resins used as a restorative material in the field of dentistry to know its advantages and disadvantages for health, aesthetics, and long-term use.

5. Conclusion
Within the limitations of this study, it can be concluded that extending the curing time can increase the DTS of bulk-fill composite resins but not the %DC or MR. However, the composition of bulk-fill composite resins not only affects its mechanical properties, %DC, and MR but also affects health, aesthetics, and longevity when used as restorative materials in dentistry. Thus, clinicians must carefully consider the composition of bulk-fill composite resins used. Among the materials investigated in this study, FBF exhibited many advantages for use as a restorative material. Its high DTS overcomes its brittleness; moreover, it has adequate polymerization and little MR, making it safe to use. This information will be useful in the future implementation of bulk-fill composite resins in dental applications.

Conflict of Interests: All authors have none to declare.

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