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Different depth-related polymerization kinetics of dual-cure, bulk-fill composites

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ABSTRACT

Objective. The aim of this study was to evaluate the polymerization kinetics qualitatively and quantitatively for dual-cure bulk-fill composites in comparison with light-cure bulk-fill and traditional incremental composites at two clinically relevant depths.

Methods. Five commercial dental composites were evaluated, including three dual-cure bulk-fill composites (BulkEZ, HyperFIL and Injectafil), one light-cure bulk-fill composite Filtek Bulk Fill Flowable (FBF) and one traditional incremental composite Filtek Z250 (Z250) as controls. Specimens were prepared in two different depths (0.5 mm and 5 mm) for 20 s light irradiation. Self-cure was also evaluated for the three dual-cure composites. The polymerization kinetics were measured continuously in real-time for at least 10 min using a Fourier-transform infrared spectroscopy (FTIR) with an attenuated total reflectance (ATR) accessory. The experimental kinetic data were fitted using two mathematical models — a sigmoidal function and a superposition of two exponential functions characterizing the gel phase and glass phase. The degree of conversion (DC) and the rate of polymerization were calculated for all test conditions.

Results. Both experimental FTIR measurements and mathematical modeling revealed distinct depth-related polymerization kinetics for BulkEZ compared to the other two dual-cure composites. Specifically, BulkEZ exhibited moderately-paced polymerization kinetics at both depths while HyperFIL and Injectafil exhibited faster polymerization at 0.5 mm and slower polymerization at 5 mm. The bulk-fill FBF and incremental Z250 exhibited relatively fast polymerization at both depths, a characteristic for light-cure. The DC values at the two depths were not significantly different for BulkEZ, but significantly higher at 0.5 mm than at 5 mm for the other four composites ($\alpha = 0.05$).

Significance. Polymerization kinetics and their depth variation for dual-cure bulk-fill composites are material dependent. The distinct depth-related polymerization kinetics revealed for BulkEZ compared to other composites may affect their contraction stress and clinical performance.

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1. Introduction

Resin-based dental restorative composites work through a process called polymerization, in which monomer molecules react with each other to form polymer chains of three-dimensional networks. Most composites are based on methacrylate resins, where the polymerization process is usually activated by applying visible light. This light-cure polymerization process is fast in the early stages where the monomer molecules are mobile and able to reach the reactive sites easily to convert into long chains. However, the polymerization rate decreases afterwards as the extent of monomer conversion increases, which hinders the mobility of monomer molecules to reach the reactive sites. The majority of the polymerization process occurs during the first few minutes after irradiation [1].

Conventional dental composites are applied in increments of 2 mm thickness to allow sufficient light penetration and photo-polymerization [2,3]. However, this is time consuming and inconvenient, especially for deep posterior cavities. The demand for a faster and simplified restorative procedure led to the development of bulk-fill composites that can be placed in a single layer of up to 4–5 mm [4]. The improved depth of cure is usually achieved through greater translucency of the material, increased photo-initiator content or an additional photo-initiator type [5]. Even with improved formula, these light-cure bulk-fill composites can still suffer from unsatisfactory polymerization at deep layers due to impeded access or attenuation of curing light [6].

Another type of composites uses chemical initiators to activate the polymerization reactions by mixing two components together. The chemical-cure process avoids the problem of insufficient photo-polymerization at deep layers. However the initiation rate of the chemical-cure composite is relatively slow because dental practitioners need enough time for setting materials, while with light-cure composites the initiation rate can be very fast and practitioners can activate the polymerization with a curing light when the materials have been perfectly settled in the cavity.

Manufacturers recently launched a new class of dual-cure bulk-fill products designed for direct restorations, such as BulkEZ (Zest Dental Solutions), HyperFIL (Parkell, Inc.) and Injectafil DC (Apex Dental Materials, Inc). They are claimed to provide unlimited depth of cure with a single layer placement. These dual-cure composites contain both light-cure and chemical-cure components: the light-cure component provides rapid, initial hardening of the top layers of the composite, stabilizing the restorations; then, the deeper layers of the composite that receive insufficient light irradiation are polymerized by the slower chemical-cure reaction. As a result, the new dual-cure composites eliminate the issues of light attenuation that would disrupt the setting of the deepest portions of the filling [7].

A key measurement of the effectiveness of polymerization is the degree of conversion (DC), which measures the percentage of carbon–carbon double bond (C=C) that is converted to carbon–carbon single bond (C—C). A high DC is vital to enhance the mechanical properties, chemical stability and longevity of the restoration [8–10]. The change of DC over time is described by polymerization kinetics, which provide critical information on the process/rate of polymerization in addition to DC. The rate of polymerization also plays an important role in the physical properties and clinical outcome of a composite. It has been documented that the rate of polymerization of a dental composite often affects its polymerization contraction stress [11]. One study demonstrated that cured composites with identical DC values could have different levels of polymerization contraction stress [12]. Another study found that a high polymerization rate could result in increased marginal gap width for the composite [13].

So far, very limited research is available investigating the polymerization kinetics of these new dual-cure composites. The aim of the present study was to evaluate the polymerization kinetics of three dual-cure bulk-fill composites in comparison with a light-cure bulk-fill composite and a traditional incremental composite at two different depths. The null hypotheses were that (a) there would be no difference in the polymerization kinetics among the investigated composites and (b) specimen depth had no effect on the polymerization kinetics of each individual composite.

2. Materials and methods

Five commercially available restorative dental composites were evaluated, including three dual-cure bulk-fill composites (BulkEZ, HyperFIL and Injectafil), one flowable light-cure bulk-fill composite Filtek Bulk Fill Flowable (FBF) and one traditional incremental composite Filtek Z250 (Z250). All three dual-cure composites have relatively low viscosity and good flowability despite their relatively high filler content (>70 wt%), eliminating the need for flowable liners. They can be light-cured or self-cured. They are designed for direct restoration with or without a top layer of capping. The chemical compositions of the five composites were listed in Table 1.

2.1. *Specimen preparation*

For light-cure test conditions, specimens were prepared in two depths (0.5 mm and 5 mm). Commercially available spacers were used as molds for specimen preparation to eliminate the need for custom fabrication. The 5 mm specimens were prepared in 5×6.3 mm black spacers (Grainger.com, Model # 13 ME069) and the 0.5 mm specimens were prepared in 0.5×24 mm black spacers (Walmart.com, Model # BB-24MM-0.5). All the specimens were prepared according to the manufacturer's instructions in a dark room at room temperature.

A Perkin-Elmer Spectrum One Fourier transform infrared spectrophotometer (FTIR) with a universal Attenuated Total Reflectance (ATR) accessory was used for the test. A LED light curing unit (3M ESPE Elipar S10, 1200 mW/cm^2, wave range 430–480 nm, Germany) was used for specimen irradiation. For light-cure testing, the molds were placed on the diamond crystal top plate of the ATR attachment with the diamond crystal in the middle. Uncured composites were filled into the molds in one increment. The specimen was immediately covered with an unbreakable plastic cover slip (Fisher brand, Catalog # 12-

Table 1 – Material information for all five composites in this study.

Composite (manufacturer)	Shade	Classification	Resin	Filler content	Particle size
Bulk EZ™ (Zest Dental Solutions)	A2	Dual-cure bulk-fill composite	BisEMA, TEGDMA, bisGMA and UDMA	Barium glass 50–70 wt% YbF3 1–20 wt%	Proprietary
HyperFIL™ DC (Parkell, Inc.)	Universal	Dual-cure bulk-fill composite	BisEMA, UDMA, and other dimetha-crylate monomers.	Barium glass/silica 70-75 wt%	15 nm–3.5 μm
Injectafil™ DC (Apex Dental Materials, Inc.)	A2	Dual-cure bulk-fill composite	BisGMA and other methacrylate resins	Silica glass, 75 wt%	Submicron to 5 μm
Filtek™ Bulk fill flowable (3M ESPE)	A2	Light-cure bulk-fill composite	BisGMA, UDMA, bisEMA, and procrylat resin	Ytterbium trifluoride and zirconia/silica fillers, 64.5 wt%	0.1–5.0 μm
Filtek™ Z250 (3M ESPE)	A2	Light-cure incremental composite	BisGMA, UDMA, and bisEMA resin	Zirconia/silica particles 82 wt%	0.01–3.5 μm

Abbreviations: BisGMA, bisphenylglycidyl dimethacrylate; BisEMA, ethoxylated bisphenol-A dimethacrylate; UDMA, urethane dimethacrylate; TEGDMA, triethylene glycol dimethacrylate.

547) and light-cured for 20 s with the tip of the curing light in contact with the cover slip. The actual irradiant power density across the cover slip was measured to be 960 mW/cm^2. For self-cure testing, the composite sample was placed directly on the diamond crystal top plate of the ATR attachment without mold or light irradiation. 3–5 specimen replicates were used for each test condition (n = 3–5).

2.2. Real-time polymerization kinetics measurement

The Spectrum TimeBase software was used to acquire the IR absorption spectra from the ATR accessary at a resolution of 4 cm^{-1} in the wavelength range between 650 and 4000 cm^{-1}. The IR spectra acquisition was manually started right before the sample placement in order to collect the spectra for uncured material. Light-curing was initiated as described above while spectra were acquired automatically in real time for at least 10 min at a basic sampling rate of one spectrum every 5.3 s. Additional higher sampling rates ranging from one spectrum every 0.4 s to one spectrum every 2 s were further used to supplement the basic measurements. A lower sampling rate generated a higher signal-to-noise ratio and less noisy kinetics curves were better for comparison and curve fitting. A higher sampling rate provided more data points for the evaluation of the fast polymerization process.

2.3. Degree of conversion calculation

In the present study, standard methods of monomer conversion analyses were used for DC calculation [14]. Baseline adjusted peak heights at 1637 cm^{-1} (aliphatic carbon double bonds) and 1608 cm^{-1} (aromatic carbon double bonds) were measured using the Spectrum TimeBase software at each time interval obtained from the FTIR spectra (Fig. 1). The absorption band 1608 cm^{-1} served as internal reference for normalization. The DC% was calculated by the reduction of normalized absorbance at 1637 cm^{-1} between uncured and cured material

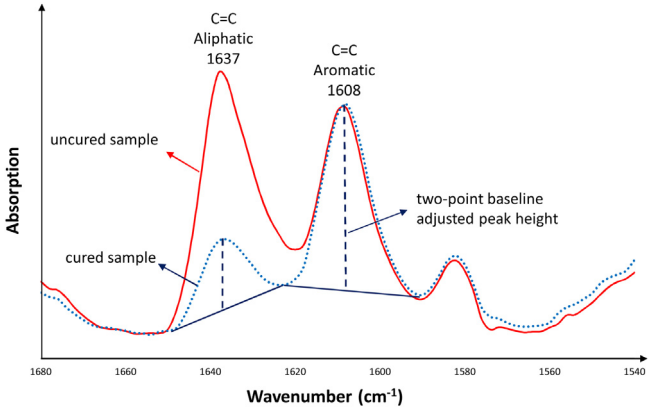

Fig. 1 – FTIR spectra in the region of interest and two-point baseline adjusted peak height at 1637 cm^{-1} and 1608 cm^{-1} for DC calculation.

using Eq. (1):

$$DC\% = \left\{1 - \frac{(1637\ cm^{-1}/1608\ cm^{-1})_{Peak\ height\ before\ cure}}{(1637\ cm^{-1}/1608\ cm^{-1})_{Peak\ height\ after\ cure}}\right\} \times 100 \quad (1)$$

The DC values from the last 10 scans at 10 min post-polymerization were used to calculate the mean and the standard deviation (SD) of DC values for all test conditions.

2.4. Mathematical modeling of polymerization kinetics

Previous studies have employed several mathematical models to describe the kinetic behavior of photo-polymerization [15–19]. These fitting functions were composed of a double component to describe the two-phase physical features of network formation. A recent study used a sigmoidal function to fit the polymerization kinetics of a dual-cure composite [20]. Since the present study involved both light-cure and dual-cure

composites, both the double-component function and the sigmoidal function were used to fit the polymerization kinetics of the five investigated composites and the quality of fit was compared between the two models. Specifically, in Model #1, the change of DC over time was described by a superposition of two exponential functions as shown in Eq. (2), in which the first exponential function was attributed to the gel phase (described by parameters a and b) and the second to the glass phase (described by parameters c and d):

$$DC = a \times \left(1 - e^{-bt}\right) + c \times \left(1 - e^{-dt}\right) \quad \text{(Model \#1)} \tag{2}$$

where the variable "t" was time and the parameters "a", "b", "c" and "d" were modulation factors of the exponential function to optimize the fit of the double exponential function to the measured DC vs. time curves. The physical meaning of each parameter could be derived from the structure of the mathematical formula that the parameters "a" and "c" were associated with the maximum DC achieved in the gel phase and in the glass phase respectively, the sum (a + c) was associated with the overall maximum DC of the composite, and the parameters "b" and "d" were associated with the rate of polymerization in the gel phase and in the glass phase respectively.

In Model #2, the change of DC over time was described by a sigmoidal model as shown in Eq. (3)

$$DC = A\frac{t^B}{C^B + t^B} \quad \text{(Model \#2)} \tag{3}$$

where the variable "t" was time and the parameters "A", "B" and "C" were modulation factors of the sigmoidal function to optimize the fit of the function to the measured DC vs. time curves. The structure of the mathematical formula suggested that the parameter "A" was associated with the maximum DC for the composite, the parameter "C" was associated with the time to reach half of the maximum DC, and therefore was inversely associated with the polymerization rate; the physical meaning of the parameter "B" was not as straightforward as "A" and "C".

For all test conditions, the change of DC over time during the 10-min post-polymerization was fitted by both Model #1 and Model #2. The Solver add-in tool in Microsoft Excel and the least-square method were used to determine best-fit parameters for each model. The coefficient of determination (r^2) was calculated to evaluate the goodness of fit, as used in previous studies [19–21]. With the coefficient of determination, the model with the higher r^2 value (up to a maximum of 1) is preferred. However, some argued that r^2 was only valid for linear regression models and it was an inadequate measure for the goodness of fit in nonlinear models. The Bayesian information criterion (BIC) was recommended alternatively [22]. Since both models in the present study were nonlinear models, the BIC was also calculated using Eq. (4) to supplement r^2 for the determination of the preferred model for a specific kinetic curve.

$$BIC = n \cdot \ln\left(\frac{RSS}{n}\right) + p \cdot \ln(n) \tag{4}$$

where n was the number of test data (sample size), p was the number of model parameters and RSS is the residual sum of squares. The criterion with BIC was that the model with lower BIC was preferred.

2.5. Rate of polymerization calculation

The rate of polymerization (RP) was calculated from the first derivative of the preferred polymerization kinetic models. The RP vs. time curves and the RP vs. DC curves at 0.5 mm and 5 mm were plotted. The peak RP values (RP_{max}) were compared among all test conditions.

2.6. Statistical analysis

Statistical analyses were performed using GraphPad Prism 5 (GraphPad Software, Inc., Version 5, San Diego, CA, USA) and Microsoft Excel 2016. Normality of data distribution was verified by Kolmogorov–Smirnov test. All DC and RP_{max} data were analyzed by 1-way or 2-way repeated measures (mixed model) analysis of variance (ANOVA) with Bonferroni post-tests for multiple comparisons ($\alpha = 0.05$). The least-square fitting method was used to determine best-fit parameter values in mathematical modeling. The coefficient of determination (r^2) and the Bayesian information criterion (BIC) were used to compare the goodness of fit between the two models.

3. Results

3.1. Polymerization kinetic curves

The real-time polymerization kinetic curves during the first 10 min post-polymerization for all five composites were summarized in Fig. 2.

Qualitative observation showed that for BulkEZ the polymerization kinetic curves were similar among two light-cure depths and self-cure, all characterized by moderately-paced increase; for HyperFIL and Injectafil, the polymerization kinetic curves were similar between 5 mm and self-cure, both characterized by relatively slow increase, versus rapid increase for the 0.5 mm curves; for FBF, the polymerization kinetic curves were similar at the two depths, both characterized by rapid increase; and for Z250, the 0.5 mm polymerization kinetic curve was characterized by a rapid increase, versus a moderately-paced increase for the 5 mm curve.

3.2. Degree of conversion (DC)

At 10 min post-polymerization, the DC values from ten consecutive scans were used to calculate the mean and standard deviation of DC for each specimen. The results were summarized in Table 2.

Analysis of the DC values of each individual dual-cure composite at two depths and in the self-cure condition using two-way mixed model ANOVA showed that for BulkEZ, the DC values were not significantly different among the two depths and self-cure conditions ($p = 0.79$); for HyperFIL, the DC values at 0.5 mm were significantly higher than the DC values at 5 mm, which were significantly higher than the DC values of self-cure ($p = 0.0004$); for Injectafil, the DC values were not significantly different between 5 mm and self-cure

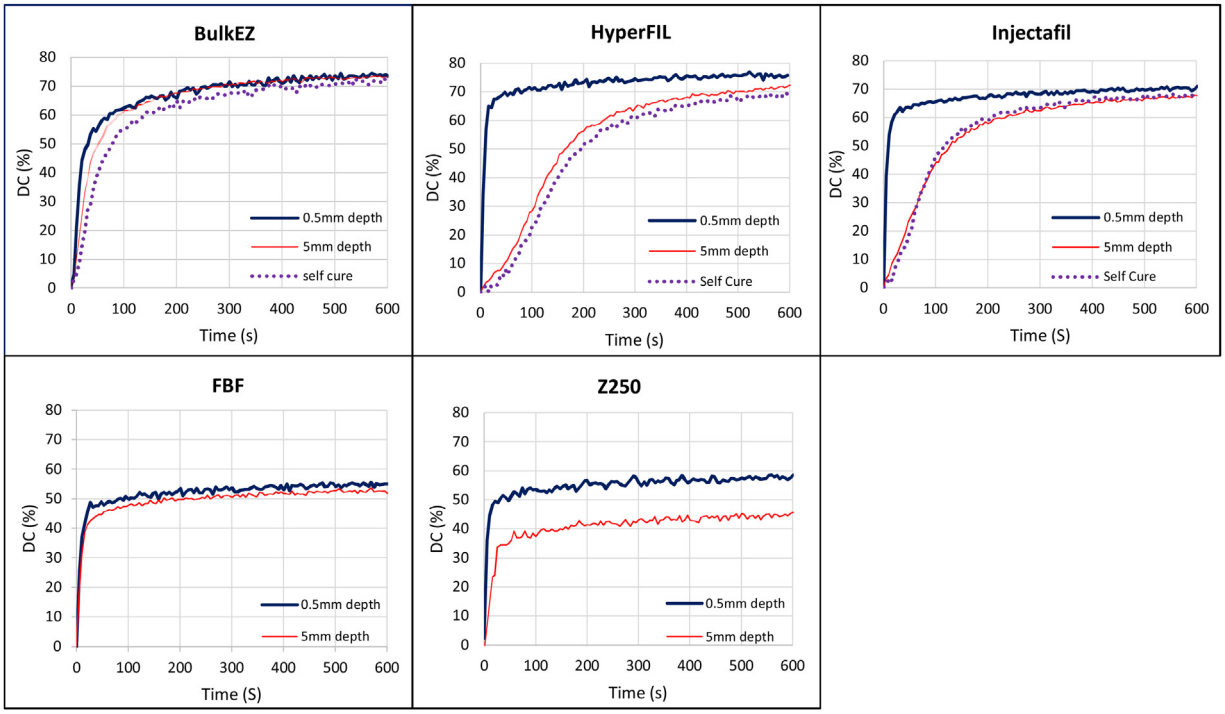

Fig. 2 – Real-time degree of conversion (DC) vs. time during 10 min post-polymerization for all five composites.

Table 2 – Degree of conversion (DC%) in mean ± SD for all test conditions.

	BulkEZ	HyperFIL	Injectafil	FBF	Z250
0.5 mm	72.39 ± 1.49	76.24 ± 1.13	70.72 ± 0.69	55.16 ± 0.95	57.05 ± 1.10
5 mm	72.33 ± 1.60	71.46 ± 0.72	68.86 ± 0.98	51.44 ± 0.92	45.52 ± 1.14
Self-cure	72.09 ± 0.53	67.90 ± 1.39	68.55 ± 0.81	N/A	N/A

N/A: not tested.

($p = 0.69$), but they were both significantly lower than the DC values at 0.5 mm ($p = 0.02$); for FBF and Z250, the DC values at 0.5 mm were significantly higher than the DC values at 5 mm ($p = 0.0063$ for FBF and $p = 0.0001$ for Z250). Comparisons of the DC values at the same depth among the five composites using one-way ANOVA showed that all five composites significantly differed in their DC values at either depth ($p < 0.01$), with the DC values of the three dual-cure composites generally higher than the DC values of FBF and Z250. Comparisons of the DC values among the five composites at both depths using two-way ANOVA showed that the composite material had a stronger influence on the degree of conversion than the specimen depth.

3.3. *Mathematical modeling*

The results of mathematical modeling for all test conditions were summarized in Table 3, including the best-fit values for the kinetic function parameters of both models, the r^2 and the BIC values of each model. Generally, both models provided good fit for the experimental data. The preferred model for each test condition was selected according to the criteria of r^2 and BIC (a larger r^2 or a smaller BIC means a better fit) and the selection results were listed in the last column of Table 3. Overall, the three dual-cure composites at 5 mm and for self-cure preferred Model #2 while other test conditions preferred Model #1, suggesting that Model #1 might be a better choice for faster polymerization kinetics and Model #2 might be a better choice for slower polymerization kinetics.

3.4. *Rate of polymerization (RP)*

The RP vs. time curves for all five composites at 0.5 mm and 5 mm were shown in Fig. 3 (the self-cure data for the three dual-cure composites were not shown in the figure due to the similarity between 5 mm and self-cure). At 0.5 mm depth (left), the polymerization initiated quickly after light-irradiation and the maximum RP occurred in the very beginning of polymerization. The RP kept decreasing to near zero at some times before 50 s for all composites. At 5 mm depth (right), the curves showed two different patterns: for the three dual-cure composites, the RP started from a lower/near zero value and climbed to a peak value (RP_{max}) and then decreased to near zero. Specifically, BulkEZ reached the RP_{max} at around 7–10 s, HyperFIL reached the RP_{max} at about 70–80 s and Injectafil reached the RP_{max} at about 10–20 s. For FBF and Z250, the 5 mm curves followed similar patterns as the 0.5 mm curves except that they started at relatively lower maximum RP values in the beginning of polymerization.

Table 3 – Comparison of polymerization kinetics parameter values between double-component function (Model #1) and sigmoidal function (Model #2) for all test conditions.

	Model #1 $DC = a \times (1 - e^{-bt}) + c \times (1 - e^{-dt})$						Model #2 $DC = A\frac{t^B}{C^B + t^B}$					PREF Model
	a	b	c	d	r^2	BIC	A	B	C	r^2	BIC	
BulkEZ (0.5mm)	47.90-52.70	0.093-0.096	20.85-22.87	0.0059-0.0062	0.992-0.994	(-45.0)-(-3.6)	76.00-78.37	0.68-0.73	12.95-16.12	0.983-0.986	52.4-70.3	1
BulkEZ (5mm)	59.54-62.27	0.027-0.028	14.53-15.38	0.0031-0.0040	0.992-0.994	39.2-179.6	74.00-75.13	1.36-1.43	31.24-34.57	0.994-0.996	5.9-99.1	2
BulkEZ (self)	62.40-63.83	0.018-0.020	18.45-25.29	0.0008-0.0011	0.993-0.994	82.6-83.8	72.63-72.70	1.44-1.50	40.03-46.53	0.996-0.996	(-4.2)-19.4	2
HyperFIL (0.5mm)	66.48-68.48	0.135-0.143	8.48-10.01	0.0043-0.0048	0.991-0.995	(-87.3)-(-35.6)	75.09-75.88	0.98-1.18	4.94-5.53	0.971-0.979	66.4-94.1	1
HyperFIL (5mm)	72.39-75.36	0.0059-0.0064	0	0	0.883-0.981	101.1-345.6	71.78-76.47	1.54-2.46	110.6-118.3	0.997-0.998	(-16.9)-35.8	2
HyperFIL (self)	69.89-73.17	0.0056-0.0078	0	0	0.984-0.992	201.9-266.1	70.26-74.37	1.53-2.04	95.53-125.4	0.994-0.998	(-22.5)-4.0	2
Injectafil (0.5mm)	58.74-63.91	0.30-0.41	8.18-11.12	0.0054-0.0071	0.989-0.993	(-96.9)-(-45.8)	71.79-74.29	0.42-0.58	0.82-1.50	0.987-0.991	(-82.6)-(-30.4)	1
Injectafil (5mm)	66.24-66.83	0.0100-0.0101	0	0	0.995-0.996	16.1-53.1	69.54-69.76	1.53-1.60	71.77-73.05	0.999-0.999	(-130.2)-(-87.1)	2
Injectafil (self)	67.95-68.65	0.0096-0.0103	0	0	0.983-0.986	222.0-223.0	68.42-69.10	1.99-2.01	71.25-76.77	0.994-0.998	(-15.1)-(-11.1)	2
FBF (0.5mm)	46.04-46.65	0.194-0.281	8.63-8.72	0.0057-0.0059	0.984-0.987	(-67.6)-(-51.6)	56.19-56.85	0.52-0.69	1.85-3.34	0.978-0.978	(-24.8)-(-6.8)	1
FBF (5mm)	40.19-43.37	0.108-0.139	9.53-10.52	0.0053-0.0061	0.993-0.995	(-154.6)-(-108.2)	51.83-53.14	0.75-0.87	6.44-7.84	0.980-0.990	(-60.7)-(-14.6)	1
Z250 (0.5mm)	48.73-49.84	0.111-0.233	7.37-8.66	0.0040-0.0060	0.981-0.986	(-46.1)-(-25.0)	56.44-60.33	0.50-0.83	1.57-3.35	0.973-0.977	(-3.2)-46.7	1
Z250 (5mm)	36.23-38.75	0.059-0.066	8.66-10.06	0.0031-0.0035	0.971-0.980	21.3-45.4	44.65-45.48	1.09-1.22	13.64-15.65	0.952-0.966	69.1-96.3	1

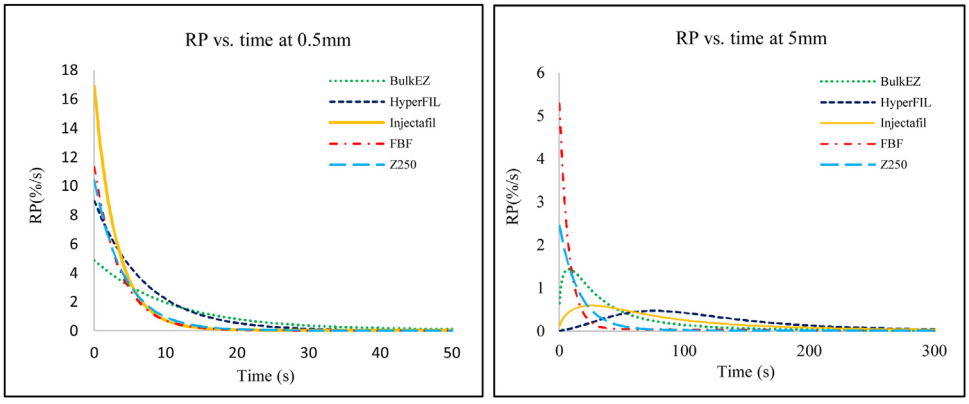

Fig. 3 – Rate of polymerization vs. time curves from preferred math models for all five composites at 0.5 mm depth (left) and at 5 mm depth (right).

The RP vs. DC curves for all five composites at 0.5 mm and 5 mm were shown in Fig. 4. For the three dual-cure composites at 5 mm, BulkEZ reached a maximum RP at around 10% DC, HyperFIL reached a maximum RP at around 20% DC and Injectafil reached a maximum RP at around 12% DC. For all other test conditions, the RP started from a maximum value in the beginning of polymerization and kept decreasing until they reached zero.

The RP_{max} values for all test conditions were summarized in Table 4. All composites showed significantly higher RP_{max} values at 0.5 mm than at 5 mm ($p < 0.001$). Among the three dual-cure composites, the RP_{max} values at the two

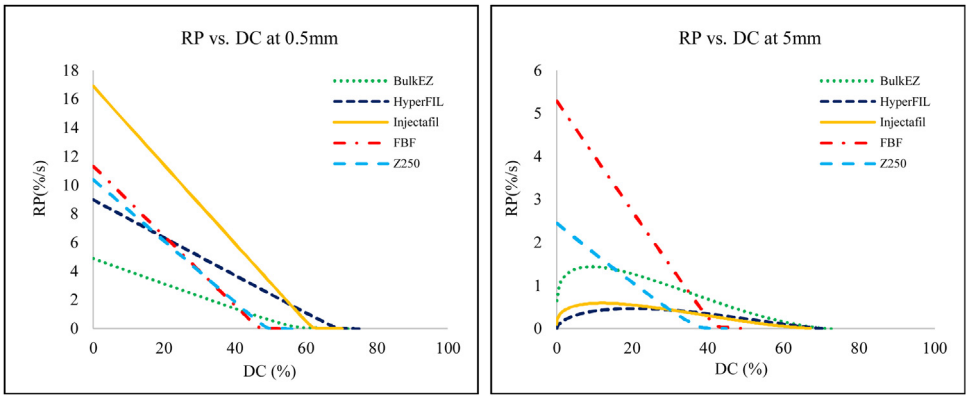

Fig. 4 – Rate of polymerization vs. DC curves from preferred math models for all five composites at 0.5 mm depth (left) and at 5 mm depth (right).

Table 4 – Maximum rates of polymerization (RP_{max}, %/s) from preferred models for all test conditions.

	BulkEZ	HyperFIL	Injectafil	FBF	Z250
0.5 mm	4.38–4.94	8.43–9.17	16.61–19.62	8.26–11.33	10.25–14.99
5 mm	1.33–1.47	0.40–0.47	0.58–0.59	4.34–5.29	2.13–2.45
Self	0.91–1.10	0.35–0.47	0.58–0.63	N/A	N/A

N/A: not applicable.

depths were much closer for BulkEZ than for HyperFIL and Injectafil.

4. Discussion

Very limited research data have been published on the polymerization kinetics of dual-cure bulk-fill composites. In the present study, the polymerization kinetics of three new dual-cure bulk-fill dental restorative composites were evaluated at two clinically relevant depths. A light-cure bulk-fill composite FBF and a traditional incremental composite Z250 were also investigated for comparisons. The results showed that polymerization kinetics of the five composites were material-related and depth-related. Therefore, our two null hypotheses were rejected.

Specifically, the FTIR results in Fig. 2 revealed distinct depth-related polymerization kinetics for BulkEZ versus HyperFIL and Injectafil. The polymerization kinetics of HyperFIL and Injectafil were depth dependent — the top layers were characterized by faster light-activated polymerization and the deep layers were characterized by slower chemical-activated polymerization, while the polymerization of BulkEZ was characterized by moderately-paced polymerization across the entire depth. In comparisons, FBF and Z250 were characterized by relatively fast light-activated polymerization up to 5 mm. Since the maximum rate of polymerization only happens at a certain moment, the overall speed of polymerization may be better described by the time it took to reach the DC plateau. In the current study, the time to reach 80% of the DC value at 10 min was used. For BulkEZ, the time was 50–80 s at 0.5 mm and 80–110 s at 5 mm; for HyperFIL and Injectafil, the time was 10–20 s at 0.5 mm and much longer (200–250 s for HyperFIL and 140–180 s for Injectafil) at 5 mm; for FBF, the time was 10–20 s at 0.5 mm and 20–40 s at 5 mm; For Z250, the time was 10–20 s at 0.5 mm and 40–50 s at 5 mm.

Mathematical modeling could serve as a useful tool to help describe the characteristics of the polymerization kinetics quantitatively. For example, in Model #1, the value of parameter "b" provided a quantitative description of the observed polymerization rate in Fig. 2. Specifically, the "b" values of more than 0.1 corresponded to the faster polymerization observed for HyperFil at 0.5 mm, Injectafil at 0.5 mm, FBF at 0.5 and 5 mm, and Z250 at 0.5 mm; the "b" values of less than 0.01 corresponded to the slower polymerization observed for HyperFIL and Injectafil at 5 mm and in their self-cure conditions; and the "b" values between 0.01 and 0.1 corresponded to the moderately-paced polymerization observed for BulkEZ in all three test conditions. The double-component math formula of Model #1 corresponds to two different phases of polymerization, the gel phase and the glass phase. The kinetic parameter results of Model #1 showed that the "a" and "b" values in the gel phase were generally larger than the "c" and "d" values in the glass phase respectively for all test conditions, suggesting more monomer conversions and higher polymerization rate in the gel phase than in the glass phase for all composites. A distinct pattern of $c = 0$ and $d = 0$ were noticed for HyperFIL and Injectafil at 5 mm and in self-cure conditions (as highlighted in Table 3), possibly suggesting that most or all monomer conversions were completed in the gel phase due to a slow polymerization rate. The four highlighted test conditions also strongly preferred Model #2 in model comparison. In reference to the literature, the parameter values of FBF in Model # 1 reported in the present study were in excellent agreement with that reported by Al-Ahdal et al. [21]. As far as we know, the present study was the first one to use two mathematical models to describe the distinct polymerization kinetics of the new dual-cure bulk-fill composites and compare them using the BIC criteria.

To our knowledge, the present study is also the first to report the DC values of the three dual-cure composites BulkEZ, HyperFIL and Injectafil. The DC values of dental composites have been widely studied and the results varied considerably among different materials. The DC values of the three dual-cure bulk-fill composites in the present study ranged from 68.55% to 76.24%, which fit into the range of 50%–86% reported in the literature for bulk-fill composites [23–27]. The DC values of FBF and Z250 in the present study ranged from 45.5%–57.1%, which are comparable to the previously reported DC values of 43.4%–58.4% for both composites under similar test conditions [26,21,28–30].

A major difference between bulk-fill composites and conventional composites is their depth of cure. As a conventional composite, Z250 has to be incrementally placed in layers of 2 mm in order to allow sufficient photo-polymerization, while the light-cure bulk-fill composite FBF is claimed to achieve an improved depth of cure of 4–5 mm. The three dual-cure bulk-fill composites are claimed to have unlimited depth of cure. A commonly accepted criteria for determining depth-of-cure is the "0.8 bottom/top ratio" for DC [31]. In the present study, the 5 mm/0.5 mm DC ratios were calculated using the mean DC values and the 0.8 ratio criteria was used to determine the efficiency of polymerization at 5 mm depth. The results showed that the 5 mm/0.5 mm DC ratio was slightly <0.80 for Z250 and about 0.93 for FBF, supporting their respective incremental and bulk-fill properties. For the three dual-cure bulk-fill composites, BulkEZ showed the same DC values among the two light-cure depths and self-cure, indicating that chemical-curing is its dominant polymerization mechanism; HyperFIL showed a 5 mm/0.5 mm DC ratio of 0.94 and a self-cure/0.5 mm DC ratio of 0.89; Injectafil showed 0.97 for both 5 mm/0.5 mm and self-cure/0.5-mm DC ratios. The results proved that all three dual-cure bulk-fill composites had unlimited depth of cure thanks to their efficient chemical-curing processes.

Compared to the widely studied degree of conversion, the polymerization kinetics such as rate is less studied in the composite literature, although it plays a very important role in the physical property and clinical performance of a dental composite. It has been well documented that the rate of polymerization of a dental composite often affects its polymerization contraction stress [11]. Polymerization contraction causes stress at the interface between a tooth substrate and a restorative composite. This stress manifests as bond failure, cuspal flexure, enamel micro-cracking, pulpal irritation and secondary caries due to bacterial infiltration, and postoperative sensitivity, which in turn can lead to restoration failure [32,33]. The contraction stress is found to be larger in light-cured composites than in chemically cured composites [13]. A lower polymerization rate of the chemical-cure process is considered as the most important factor contributing to the observed lower polymerization contraction stress [34–37]. A possible underlying mechanism is that a slower polymerization process delays the gel point and allows more resin to flow from the unbounded (free) surface, which in turn reduces the shrinkage from the bonded area [34,36]. Similar explanation was also given by Braga et al. that in a slower polymerization reaction, the viscous phase is prolonged and the material molecules can easily rearrange and dissipate some of the tensions generated by the contraction [38]. It has been commonly observed that slower chemical-cured composites have better marginal adaptation and present less damage to the integrity of the restored tooth than their faster light-cured counterparts [39–41].

Since the rate of polymerization affects the contraction stress of a composite, different polymerization rates revealed in the present study for the three dual-cure composites will likely have interesting implications for their physical properties and clinical performance. BulkEZ has a moderately-paced polymerization across the entire depth and the time to reach the conversion plateau is similar at 0.5 mm and at 5 mm. As a result, different layers will likely reach rigidity in similar time frames (about 1–2 min) and experience similar moderate contraction stress. For HyperFIL and Injectafil, the time to reach the conversion plateau is about 10 times longer at 5 mm than at 0.5 mm. When the top layers complete most of its polymerization reactions and reach rigidity after 20 s, the deep layers still exhibit ongoing reactions and are viscous. The fast-cured top layers are likely to have higher contraction stress on tooth substrates as other light-cure composites while the slowly-cured deep layers are likely to produce lower contraction stress.

More studies are needed to experimentally measure the polymerization contraction stress of these dual-cure composites and to better understand how the difference in polymerization kinetics affect their physical properties (restoration integrity, marginal gaps, micro-leakages etc.). Further research to evaluate the long-term clinical performance of these dual-cure composites is also desired.

5. Conclusion

The three tested dual-cure bulk-fill composites exhibited different depth-related polymerization kinetics. Specifically, BulkEZ is characterized by moderately-paced polymerization kinetics across the entire depths while HyperFIL and Injectafil are characterized by fast light-cure polymerization in top layers and slow chemical-cure polymerization in deep layers. The difference in polymerization kinetics may have interesting implications for their physical properties and clinical performance.

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