Raman Spectroscopic Assessment of Degree of Conversion of Bulk-Fill Resin Composites – Changes at 24 Hours Post Cure

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Raman Spectroscopic Assessment of Degree of Conversion of Bulk-Fill Resin Composites – Changes at 24 Hours Post Cure

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Clinical Relevance

Degree of conversion (DC) affects various physical properties and biocompatibility of a composite restoration. Adequate DC is especially important for bulk-fill materials, which are designed for placement in thick layers.

SUMMARY

Objective: The aim of this study was to determine degree of conversion (DC) of solid and flowable bulk-fill composites immediately and after 24 hours and investigate the variations of DC at surface and depths up to 4 mm.

Materials and Methods: Eight bulk-fill composites (Tetric EvoCeram Bulk Fill [shades IVA and IVB], Quixfil, X-tra fil, Venus Bulk Fill, X-tra Base, SDR, Filtek Bulk Fill) were investigated, and two conventional composites (GrandioSO, X-Flow) were used as controls. The samples (n = 5) were cured for 20 seconds with irradiance of 1090 mW/cm^2. Raman spectroscopic measurements were made immediately after curing on sample surfaces and after 24 hours of dark storage at surface and at incremental depths up to 4 mm. Mean DC values were compared using repeated measures analysis of variance (ANOVA) and *t*-test for dependent samples.

Results: Surface DC values immediately after curing ranged from 59.1%-71.8%, while the 24-hour postcure values ranged from 71.3%-86.1%. A significant increase of DC was observed 24 hours post cure for all bulk-fill composites, which amounted from 11.3% to 16.9%. Decrease of DC through depths up to 4 mm varied widely among bulk-fill composites and ranged from 2.9% to 19.7%.

Conclusions: All bulk-fill composites presented a considerable 24-hour postcure DC increase and clinically acceptable DC at depths up to 4

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mm. Conventional control composites were sufficiently cured only up to 2 mm, despite significant postcure polymerization.

INTRODUCTION

A continuing evolution of dental resin composites has led to the development of bulk-fill materials. In a wide variety of commercial materials, bulk-fill composites have drawn particular attention due to proposed placement of thick layers up to 4 mm. Apart from the clinically relevant time-savings, bulk placement can prevent void incorporation and contamination between layers, resulting in a more compact filling. Less air entrapment might also improve the degree of conversion (DC) due to decreased oxygen inhibition.[1]

On the other hand, bulk placement raises concerns regarding the depth of cure as well as the effect of a high volume of contracting material on polymerization shrinkage. It has been demonstrated that placement in incremental oblique layers produces less shrinkage stress because individual layers have higher unbonded surface, thus virtually reducing the Configuration-factor of an individual layer.[2] Also, the DC of conventional composites decreases rapidly at depths over 2-3 mm due to light attenuation and insufficient activation of the photoinitiator system.[3] Manufacturers of the bulk-fill composites claim that these materials have sufficiently reduced polymerization shrinkage stress and improved depth of cure, so that they are suitable for placement in layers up to 4 mm. This is attained by various strategies, eg, by increasing material translucency by using macrofillers,[4] introducing particles with low elastic modulus,[5] modifying resin composition,[6,7] or by using alternative photoinitiator systems.[4,5] Several studies have supported favorable properties of bulk-filling composite materials. Adequate depth of cure,[8,9] reduced cuspal deflection in comparison to conventional composites,[10] and a good marginal integrity[11] have been demonstrated for some bulk-fill composites. Although these individual composites performed well, the properties of the whole group of bulk-fill materials should be investigated further.

Adequate DC is clinically significant because it affects virtually every physical property—strength, hardness, elastic modulus, dimensional stability, solubility, water sorption, and color stability[12]—as well as biocompatibility.[13] Higher DC implies larger polymeric molecules that yield better physical properties and less free monomer that may leach from the restoration and potentially exert cytotoxic and genotoxic effects.

The efficiency of curing decreases progressively with increasing depth. As the curing light is attenuated by the absorption and scattering at increasing depths,[14] fewer free radicals are formed to initiate the polymerization. This problem has been addressed under the term depth of cure, which refers to a layer of thickness that is adequately cured, while it remains unclear how to define the "adequate" cure. For convenience, it has been determined as a depth at which the microhardness value equals the surface value multiplied by 0.8. This definition of "adequate" cure is being questioned by some investigators who propose different methods for determination of depth of cure.[15] Another classical method for determining the depth of cure, the ISO 4049 method, is still used but has been demonstrated to overestimate the depth of cure of bulk-fill composites.[16]

Conventional composite materials usually reach a DC of about 50%-75%.[17,18] For bulk-fill materials, DC values ranging from 50%-79% have been reported.[7,19] Some authors suggest a DC of 55% as a minimal value for clinical success.[19] Although the exact threshold DC value required for clinical success of a restoration cannot be determined, DC is a useful predictor of a restoration's physical and mechanical properties, as well as biocompatibility. Furthermore, comparing the DC at various depths may be helpful for assessment of curing efficiency, which decreases with increasing depth.[20]

To assess the DC, direct and indirect methods can be used. Direct methods based on vibrational spectroscopy are considered more accurate because they directly quantify the amount of unreacted C=C bonds.[21] Indirect methods of DC determination correlate the DC and microhardness values and may prove inaccurate.[22] Although Fourier transform infrared (FTIR) spectroscopy has been traditionally used for DC assessment, Raman spectroscopy provides an alternative method that may, in some experimental designs, prove simpler and more adaptive than FTIR.[23] Sample preparation for Raman spectroscopy has no specific requirements, and the sample can be used as-made, ie, no additional sample processing is required.[23] In addition to easier sample handling, Raman also enables multiple measurements on the same sample due to the nondestructive sample preparation. While FTIR spectroscopy measures the absorption of incident radiation, Raman is based on the inelastic scattering phenomenon. Molecules in the sample are excited to a virtual energy state by laser light and then relaxed to a molecular vibrational state followed by emission of photons with energy different from energy of the incident photon. A Raman photon is emitted if a molecule undergoes a transition to a higher vibrational energy state than its original state (Stokes-Raman), or to a lower energy vibrational state (Anti-Stokes Raman). The energy spectrum of emitted photons is determined by vibrational energy states that are characteristic for specific functional groups and chemical bonds. As in FTIR spectroscopy, the band at 1640 cm^{-1} is assigned to the vibrations of C=C bonds and its relative change in intensity before and after curing is used to calculate the DC. When used for the DC assessment of dental composites, Raman and FTIR spectroscopy yield similar results.[23]

The aim of this study was to determine the DC of solid and flowable bulk-fill composites and investigate the variations of DC at the surface and at four clinically relevant depths, using conventional composites as controls. DC was determined using Fourier transform-Raman (FT-Raman) spectroscopy immediately after curing and after 24 hours of dark storage at 37°C. The null hypotheses were: 1) there is no difference between the DC values immediately after curing and 24 hours after curing, 2) there is no difference in the DC values between various depths for a given material, and 3) there is no difference in the DC values between various materials for a given depth.

METHODS AND MATERIALS

The composite materials used are listed in Table 1. Conventional composites GrandioSO (VOCO, Cuxhaven, Germany) and X-Flow (Dentsply, York, PA, USA) were used as controls for solid and flowable bulk-fill composites, respectively.

Five samples were made for each composite material (n=5). For sample preparation, a custom-made cylindrical stainless steel split-mold with an aperture diameter of 3 mm and depth of 6 mm was used. Uncured composite material was applied into the mold, the mold aperture was covered with a polyethylene terephthalate (PET) film, and curing was performed with a LED curing unit, Bluephase G2 (Ivoclar Vivadent, Schaan, Liechtenstein), for 20 seconds with irradiance of 1090 mW/cm^2 ("high" mode). The irradiance of the curing unit was tested with a Cure Rite radiometer (Caulk Dentsply, Konstanz, Germany) before each composite material. The variations were under 10%, and the value of 1090 mW/cm^2 represents the arithmetic mean of 10 measurements. The curing time of 20 seconds corresponds to or exceeds the manufacturer's recommendations for all tested materials. The curing unit tip was positioned at the angle of 90°, immediately adjacent to the mold aperture, contacting the PET film covering the sample. Sample curing was done at 21°C ± 1°C and 60% ± 15% relative humidity. Immediately after curing, Raman spectra were collected from the sample surfaces. The samples were then placed in an incubator (Cultura, Ivoclar Vivadent) at 37°C ± 1°C and 90% ± 10% relative humidity. After a dark storage period of 24 hours, Raman spectra were collected from five depths: 0 mm (surface), 1 mm, 2 mm, 3 mm, and 4 mm.

FT-Raman spectroscopy measurements were performed using a Spectrum GX spectrometer (Perkin-Elmer, Waltham, MA, USA). The excitation was a Nd:YAG laser at 1064 nm wavelength, with laser power of 800 mW and resolution of 4 cm^{-1}. The samples were mounted on a universal holder that enabled translation along the cylindrical sample, thereby exposing different depths to the excitation laser light. During the measurement, the exposed sample surface was about 0.5 mm in diameter. For each spectrum, 100 scans were recorded. Spectra of the uncured composites (n=5) were recorded in the same manner. The spectra were processed with the Kinetics add-on for Matlab (Mathworks, Natick, MA, USA).

DC calculation was performed by comparing the relative change of the band at 1640 cm^{-1}, representing the C=C stretching mode to a reference band, before and after the polymerization. For GrandioSO, Tetric EvoCeram Bulk Fill, Quixfil, X-tra fil, Venus Bulk Fill, X-tra Base, and Filtek Bulk Fill, the aromatic C=C band at 1610 cm^{-1} was used as a reference. Due to the lack of the aromatic C=C stretching mode in the case of SDR and X-Flow, reference bands at 1600 cm^{-1} and 1458 cm^{-1} (C-H stretching mode) were used, respectively.[19,24] Integrated intensities of C=C and reference bands were used for DC calculation by the following equation: $DC = 1 - R_{polymerized}/R_{unpolymerized}$, where R = (C=C band area)/(reference band area).[21] The normality of distribution of residuals was verified using the Shapiro-Wilk test. DC values obtained from multiple depths 24 hours post cure were compared using repeated measures analysis of variance (ANOVA) and Benjamini-Hochberg adjustment for multiple comparisons. Surface DC values obtained immediately after curing were compared to the surface values obtained 24 hours post cure using a dependent samples *t*-test. Statistical analysis was made in SAS (SAS Institute, Cary, NC, USA); *p*-values lower than 0.05 were considered statistically significant.

Table 1: ***Manufacturers' Information About the Composite Materials Used***

Type	Composite Material (Manufacturer)	Shade/Lot (expiration date)	Composition	Filler Amount, wt%/vol%
Conventional solid	GrandioSO (VOCO, Cuxhaven, Germany)	A2/1222126 (2014/11)	Inorganic fillers in a methacrylate matrix (Bis-GMA, TEGDMA)	89/73
Conventional flowable	X-Flow (Dentsply, York, PA, USA)	A2/1206001145 (2014/05)	Sr-Al-Na-F-P silicate glass, difunctional and multifunctional acrylate and methacrylate resins, diethylene glycol dimethacrylate, highly dispersed silicon dioxide, ultraviolet (UV) stabilizer, ethyl-4-dimethylaminobenzoate, camphorquinone, butylated hydroxy toluene, iron pigments, titanium dioxide	60/38
Bulk-fill solid	Tetric EvoCeram Bulk Fill IVA (Ivoclar Vivadent, Schaan, Liechtenstein)	IVA/P82299 (2015/12)	Dimethacrylates: Bis-GMA, Bis-EMA, UDMA, barium glass, ytterbium trifluoride, mixed oxide and prepolymer; additives, catalysts, stabilizers, pigments	81/61
	Tetric EvoCeram Bulk Fill IVB (Ivoclar Vivadent, Schaan, Liechtenstein)	IVB/R77065 (2016/10)		
	Quixfil (Dentsply, York, PA, USA)	Universal/ 121200233 (2014/05)	UDMA, TEGDMA, dimethacrylate and trimethacrylate resins, carboxylic acid modified dimethacrylate resin, butylated hydroxy toluene (BHT), UV stabilizer, camphorquinone, ethyl-4-dimethylaminobenzoate, silanated strontium aluminum sodium fluoride phosphate silicate glass	86/66
	X-tra fil (VOCO, Cuxhaven, Germany)	U/1311472 (2015/03)	Inorganic filler in a methacrylate matrix (Bis-GMA, UDMA, TEGDMA)	86/70
Bulk-fill flowable	Venus Bulk Fill (Heraeus Kulzer, Hanau, Germany)	Universal/010030 (2014/07)	Multifunctional methacrylate monomers (UDMA, EBADMA), Ba-Al-F silicate glass, YbF_3, SiO_2	65/38
	X-tra Base (VOCO, Cuxhaven, Germany)	Universal/1310503 (2015/06)	Inorganic fillers in a methacrylate matrix (aliphatic dimethacrylate)	75/61
	SDR (Dentsply, York, PA, USA)	Universal/ 1301001101 (2014/12)	Ba-Al-F-B silicate glass, Sr-Al-F silicate glass, modified UDMA, ethoxylated bisphenol A dimethacrylate (EBPADMA), TEGDMA, camphorquinone, photoaccelerator, BHT, UV stabilizer, titanium dioxide, iron oxide pigments, fluorescing agent	68/45
	Filtek Bulk Fill (3M ESPE, Saint Paul, MN, USA)	A3/N502066 (2016/02)	Bis-GMA, UDMA, Bis-EMA, Procrylat resin, ytterbium trifluoride, zirconia/silica	65/43

Abbreviations: Bis-EMA/EBADMA: ethoxylated bisphenol-A-dimethacrylate; Bis-GMA: bisphenol-A-glycidylmethacrylate; TEGDMA: triethylene glycol dimethacrylate; UDMA: urethane dimethacrylate.

RESULTS

Mean DC values are presented in Figure 1 and Table 2. Decrease of DC through depths is presented as a given-depth/top ratio in Figure 2.

Statistical analysis revealed a significant 24-hour post cure increase in DC for all composites. Within the same material, statistical analysis showed significant differences between the surface/4 mm and 1 mm/4 mm DC values.

Conventional composites GrandioSO and X-Flow demonstrated a considerable decrease of DC at 3-mm and 4-mm depth, while DC decrease of bulk-fill composites was notably lower. Among bulk-fill composites, Tetric EvoCeram Bulk Fill IVA and IVB demonstrated the most pronounced DC decrease through depths, while Venus Bulk Fill and SDR showed the lowest DC decrease through depths.

The influence of different shades on DC was assessed by comparing the IVA and IVB shades of Tetric EvoCeram Bulk Fill. Significantly lower DC of shade IVB was found only at 4-mm depth, while differences at other depths were not significant.

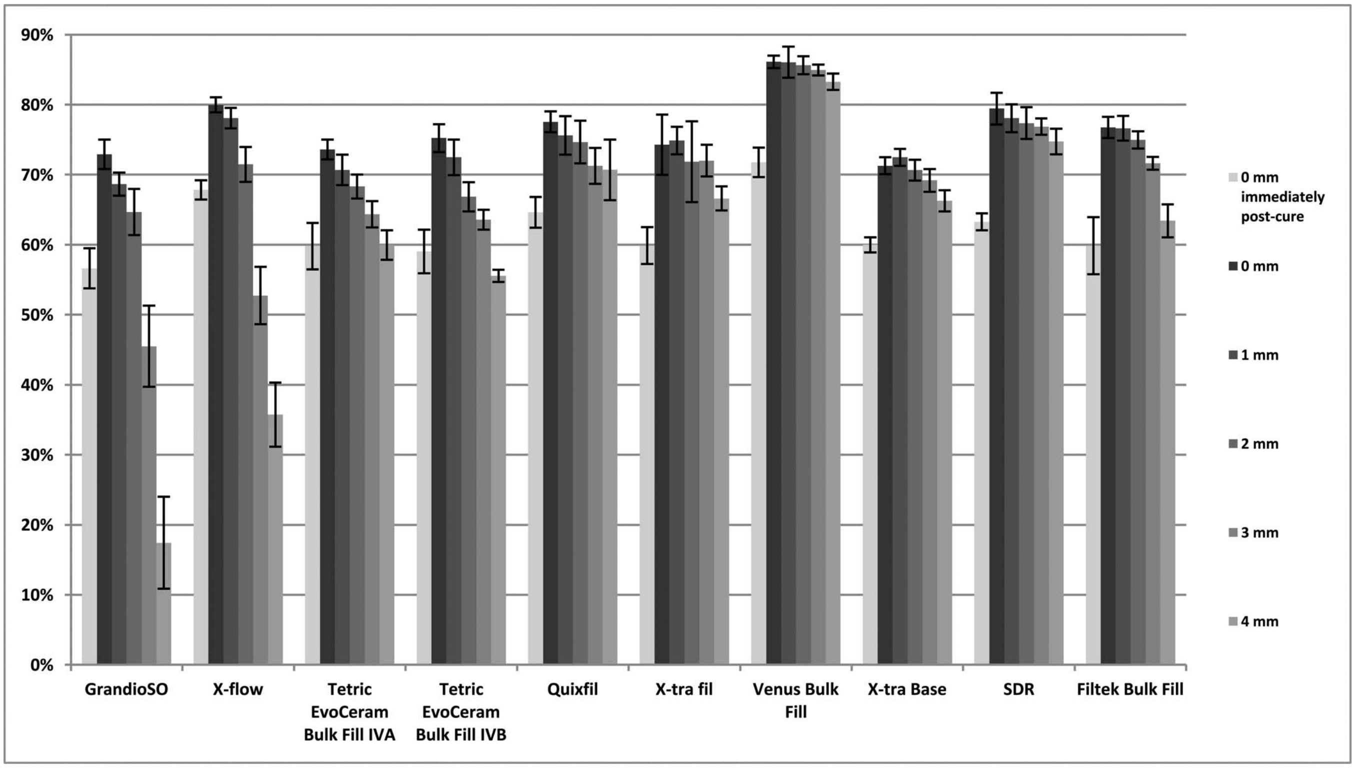

Figure 1. *Mean degree of conversion values ±SD.*

DISCUSSION

The present study was performed to determine the DC of the majority of currently available commercial bulk-fill composites by means of Raman spectroscopy. Additionally, the development of DC measured immediately and 24 hours post cure, decrease in DC through different depths up to 4 mm, between-material differences at individual depths, and differences in DC between two composite shades were observed.

Methodology

Raman spectroscopy is often used as an alternative to FTIR for determination of the DC of composite materials. An important advantage of Raman spectroscopy is the nondestructive sample preparation,

Table 2: ***Mean Degree of Conversion Values Immediately After Curing and 24 Hours Post Cure at Five Measuring Depths (n=5)***

Composite material	Immediately After Curing		24 Hours Post Cure									
	0 mm (Surface)		0 mm (Surface)		1 mm		2 mm		3 mm		4 mm	
	Mean, %	SD	Mean, %	SD	Mean, %	SD	Mean, %	SD	Mean, %	SD	Mean, %	SD
GrandioSO	56.6*	2.9	72.9* ^{Aac}	2.1	68.6 ^{ABacg}	1.7	64.7 ^{Ba}	3.3	45.5 ^{Ca}	5.8	17.4 ^{Da}	6.6
X-Flow	67.8*	1.4	80.0* ^{Ab}	1.1	78.1 ^{Ab}	1.5	71.5 ^{Bbe}	2.5	52.7 ^{Cb}	4.1	35.7 ^{Db}	4.6
Tetric EvoCeram Bulk Fill IVA	59.8*	3.3	73.6* ^{Aa}	1.4	70.7 ^{Bacd}	2.2	68.3 ^{Bcd}	1.7	64.4 ^{Cc}	1.9	60.0 ^{Dc}	2.1
Tetric EvoCeram Bulk Fill IVB	59.1*	3.1	75.2* ^{Aad}	2	72.5 ^{Bdef}	2.5	66.9 ^{Cad}	2.1	63.6 ^{Dc}	1.4	55.6 ^{Ed}	0.9
Quixfil	64.6*	2.2	77.6* ^{Abd}	1.5	75.6 ^{Abe}	2.7	74.7 ^{ABefg}	3.0	71.3 ^{Bdf}	2.6	70.7 ^{Be}	4.3
X-tra fil	59.9*	2.6	74.3* ^{Aace}	4.3	74.9 ^{Abf}	2	71.9 ^{Abcf}	5.8	72.0 ^{Adf}	2.3	66.6 ^{Bei}	1.7
Venus Bulk Fill	71.8*	2.1	86.1* ^{Af}	0.9	86.1 ^{Ag}	2.2	85.6 ^{Ah}	1.3	85.0 ^{ABe}	0.8	83.3 ^{Bf}	1.2
X-tra Base	60.0*	1.1	71.3* ^{Ac}	1.2	72.5 ^{Adfg}	1.2	70.7 ^{ABb}	1.5	69.2 ^{Bf}	1.6	66.3 ^{Cg}	1.5
SDR	63.3*	1.2	79.5* ^{Ab}	2.3	78.1 ^{Ab}	2	77.4 ^{ABg}	2.3	76.9 ^{ABg}	1.2	74.7 ^{Bh}	1.8
Filtek Bulk Fill	59.9*	4.1	76.8* ^{Ade}	1.5	76.6 ^{Ab}	1.8	75.0 ^{Af}	1.2	71.6 ^{Bd}	0.9	63.4 ^{Ci}	2.3

** Statistically significant differences between surface DC values immediately after curing and 24 hours post cure. For DC values obtained 24 hours post cure, same uppercase letters indicate statistically similar groups in rows and same lowercase letters indicate statistically similar groups in columns.*

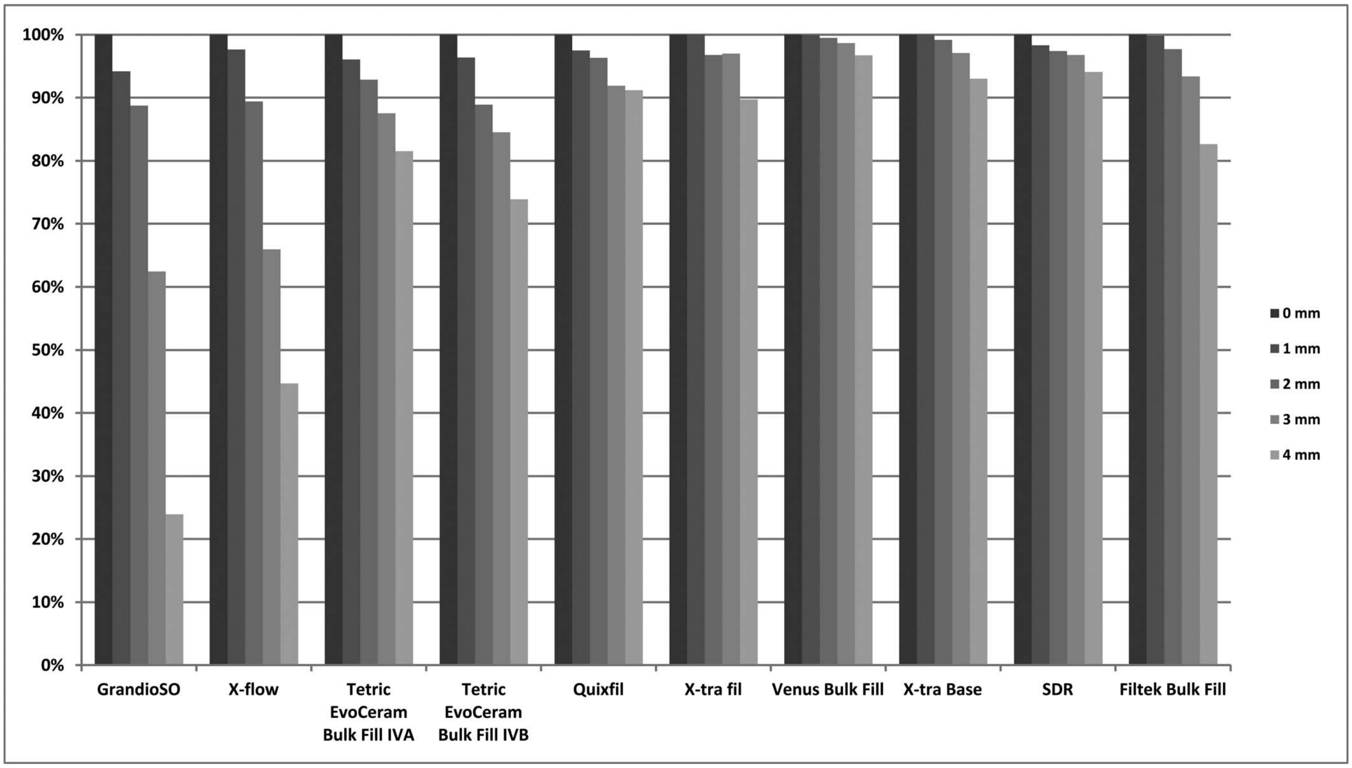

Figure 2. *Decrease of degree of conversion through depths presented as a given-depth/top ratio.*

which enabled multiple measurements at various depths on the same sample. Unlike FTIR, Raman is insensitive to eventual water contamination, which allowed for the samples to be kept in an incubator at 37°C ± 1°C and 90% ± 10% relative humidity during the 24-hour storage period in an attempt to better reproduce conditions in the oral cavity.

FTIR spectroscopy was used in a recent study examining the DC of bulk-fill composites.[19] In that study, recorded surface DC values for SDR, Venus Bulk Fill, X-tra Base and GrandioSO were consistently lower than in the present work. The difference can be ascribed to lower curing light irradiance (halogen curing unit of 600 mW/cm^2 vs polywave LED curing unit of 1090 mW/cm^2). However, the DC rankings obtained were concurrent, with the DC surface values decreasing in the following order: Venus Bulk Fill > SDR > GrandioSO > X-tra Base. This demonstrates the comparability of the results despite the differences in curing conditions and methodology used (Raman vs FTIR).

Surface DC Immediately Post Cure and 24 Hours Post Cure

The first hypothesis was rejected, since a substantial postcure increase in the DC values at the surface of the samples was noted. This effect is already well known in conventional resin composites,[25-27] but only one study showed it in flowable bulk-fill materials.[19] According to Burtscher,[28] even a small increase in the extent of DC near the end of the polymerization process can largely affect the density of cross-linking in the polymer network, and thus the mechanical properties (hardness and elastic modulus) of resin composites.[26] Postpolymerization was found to be more pronounced in samples with initially lower DC. Namely, in highly polymerized samples, reactive sites are immobilized in the polymer network, whereas in samples with initially lower DC, a higher amount of unreacted radicals allows for the increased mobility to make contact with other reactive species in the polymer network.[26]

DC increase after 24 hours of dark storage at 37°C amounted to 11.3% (X-tra Base) to 16.9% (Filtek Bulk Fill) and was statistically significant for both bulk-fill and conventional composites. Some of the previous studies were inconclusive regarding the extent of postcure polymerization,[29,30] but one study[19] has reported a considerable increase in DC of bulk-fill composites. The continuation of polymerization after curing may affect the comparability of DC values reported in various studies, since DC measurements can be performed at different postcure times.[7,19]

A previous study has assessed surface DC values for GrandioSO, Venus Bulk Fill, X-tra Base, SDR, and Filtek Bulk Fill immediately after polymerization and 24 hours post cure.[19] Both the DC values recorded immediately after curing and 24 hours post cure were slightly lower than those obtained in our study. This can be attributed to lower curing radiant exposure (20 seconds at 600 mW/cm^2). Moreover, the previous study[19] reported more extensive postcure DC increase for GrandioSO, Venus Bulk Fill, and SDR than recorded in our study, which can be explained by the finding that the amount of postcure polymerization is higher in samples that received lower radiation doses.[25]

X-tra Base demonstrated the lowest postcure DC increase and the lowest DC values up to 3 mm depth of all flowable materials. Filler load of X-tra Base amounts for 61 vol%, which is in the range of some solid bulk-fill composites, namely Tetric EvoCeram Bulk Fill (Table 1). High filler amounts may impair the mobility of reactive sites and in turn decrease the DC.[31,32] This might also be one of the reasons for somewhat lower postcure increases in DC. Also, high filler load may additionally contribute to lower DC at depth by decreasing a composite's translucency.[4] However, a conclusive answer cannot be given at this time since the exact resin composition is not provided.

The highest postcure DC increase was observed for SDR and Filtek Bulk Fill. SDR contains a patented modified UDMA, which is claimed to reduce polymerization shrinkage and shrinkage stress.[6] Similarly, Filtek Bulk Fill contains a proprietary monomer analogous to Bis-GMA and patented as Procrylat resin.[33] It is possible that these modified monomers have altered polymerization kinetics and delayed the monomer conversion, which could explain higher postcure DC increase.

From a clinical standpoint, a rather high postcure DC increase implies that restorations do not develop their final mechanical properties immediately after curing. Upon continuing postcure polymerization, mechanical properties gradually increase up to (at least) 24 hours post cure. The results of this study stress the importance of timing as a consequential factor, which should be taken into account in scientific investigations of bulk-fill composites. Assessment of DC, as well as other properties affected by DC, should be made at standardized postcure times (eg, after 24 hours) to ensure comparability to other studies.

DC at Various Depths 24 Hours Post Cure

Surface DC values of bulk-fill composites measured 24 hours post cure ranged from 71.3% (X-tra Base) to 86.1% (Venus Bulk Fill), which fits or slightly exceeds the previously reported DC range of conventional[17] and bulk-fill composites.[7,19]

Successive measurements at various depths were made to assess the influence of increasing depth of cure efficiency, since the decrease of DC at depth is inevitable due to light attenuation.[15] For tested bulk-fill composites, surface/4 mm DC decrease ranged from 2.9% (Venus Bulk Fill) to 19.7% (Tetric EvoCeram Bulk Fill IVB), and for most bulk-fill composites (Quixfil, X-tra fil, Venus Bulk Fill, X-tra Base, SDR) amounted to less than 10%. In comparison, DC of conventional composites GrandioSO and X-Flow decreased at 4 mm depth for 55.5% and 44.3%, respectively. Thus, bulk-fill composites presented improved curing efficiency at depth, which supports manufacturers' recommendations for placement of 4-mm layers.

Within the same material, DC values at 4 mm were significantly lower than surface and 1 mm values for all tested composites. Hence, the second hypothesis was rejected. However, for most of the bulk-fill composites, the surface/4 mm differences were well below 10%, which can be considered clinically acceptable. Statistical significance that was noted for some of the clinically negligible differences (amounting to 2%-4%) was due to low standard deviations. The statistical heterogeneity between individual depths was most pronounced in Tetric EvoCeram Bulk Fill IVA and IVB. In the group of solid bulk-fill composites, Tetric EvoCeram Bulk Fill also demonstrated the highest DC decrease at depth, which may be due to its higher opacity in comparison to other bulk-fill composites.[4] Among the flowable bulk-fill composites, the highest DC decrease at depth was observed for Filtek Bulk Fill. Filtek Bulk Fill differs from other materials in this study by containing zirconia filler, which was shown to decrease translucency due to resin/filler refractive index mismatch.[34] Lower translucency of Filtek Bulk Fill in comparison to most available bulk-fill materials was also reported by Bucuta and Ilie.[4]

Differences in light penetration through composite material may be attributed to the light scattering at the filler-resin interfaces and absorbance by photoinitiators and pigments.[35] Thus, the curing efficiency at increasing depths is affected by the filler composition, which determines the light attenuation. Some of the tested bulk-fill materials (Tetric EvoCeram

Bulk Fill IVA and IVB, Filtek Bulk Fill) are notably less translucent than the other bulk-fill materials tested.[4] Differences in translucence affected the DC decrease at depth, as can be seen by comparing the 4-mm/surface DC ratios.[20] Three composites with higher opacity (Tetric EvoCeram Bulk Fill IVA and IVB, Filtek Bulk Fill) show 4-mm/surface ratios of 81%, 74%, and 83%, respectively, while the other bulk-fill composites show ratios equal to or higher than 90% (Figure 2). On the other hand, their opacity gives them advantage over other bulk-fill composites in terms of acceptable esthetics for placement in the visible zone, eg, mesial class II restorations.

The third hypothesis was also rejected; in multiple comparisons of the DC values at the same depth, statistical analysis revealed significant differences between some of the tested materials. Generally, more statistical heterogeneity was observed at greater depths, ie, at 3 mm and 4 mm. Since the DC of a composite material depends on multiple intrinsic factors,[12] the observed between-material differences are expected. Also, the differences became more apparent at greater depths due to differences in light attenuation and efficiency of photoinitiator system in various bulk-fill composites.

A study by Bucuta and Ilie[4] assessed the light transmittance and microhardness of bulk-fill composites. The transmittance values at 4 mm depth were decreasing in the following order: Venus Bulk Fill > SDR > X-tra Base > Filtek Bulk Fill. In our study, the same ranking for DC values at 4 mm depth 24 hours post cure was obtained, with statistically significant differences among all four materials. Thus, DC of flowable bulk-fill composites at a maximal recommended depth of 4 mm appears to be highly dependent on the material's translucency.

Venus Bulk Fill showed the highest DC values and the lowest DC decrease at depth of all tested bulk-fill composites. This can be the result of relatively low filler load (38 vol%) and very high translucency.[5] Although Venus Bulk Fill attains very high DC, low filler loading may impair mechanical properties.[8,16] The load-bearing capability of the restoration could be improved by placing an additional 2-mm layer of universal/posterior composite over the Venus Bulk Fill core, as recommended by the manufacturer.

A possible influence of different shades of Tetric EvoCeram Bulk Fill (IVA and IVB) on DC was investigated. For a given irradiation dose, DC of a composite is determined by resin formulation, photoinitiator system, filler load, and filler morphology.[36] Additionally, composite translucency plays an important role in DC decrease at depth.[4] Based on the manufacturer's information, it can be assumed that both shades of Tetric EvoCeram Bulk Fill have the same photoinitiator system as well as resin and filler composition, differing only by a low number of pigmented particles that are used to adjust the shade. These particles are responsible for the curing light attenuation and might influence the DC at depth. The differences in attenuation between two shades are expected to become more pronounced as the distance of light path increases. IVA shade showed significantly higher DC than IVB shade at 4 mm depth, while no significant difference was observed at other depths. It appears that the light path of 4 mm is required for differences in light attenuation due to different shades to reflect as a difference in DC.

CONCLUSIONS

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

1) All tested bulk-fill composites presented a considerable 24-hour postcure DC increase, up to 16.9%.
2) All tested bulk-fill composites presented clinically acceptable DC at depths up to 4 mm.
3) Differences between surface DC and 4-mm DC values varied widely among bulk-fill composites (2.9% for Venus Bulk Fill to 19.7% for Tetric EvoCeram Bulk Fill IVB). For most of the bulk fill composites, the difference was under 10%.

In this study, all tested bulk-fill composites performed adequately with respect to DC. Further study investigating other properties is needed to advocate their clinical use.

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Conflict of Interest

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

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REFERENCES

1. Gauthier MA, Stangel I, Ellis TH, Zhu XX (2005) Oxygen inhibition in dental resins *Journal of Dental Research* **84**(**8**) 725-729.
2. Park J, Chang J, Ferracane J, Lee IB (2008) How should composite be layered to reduce shrinkage stress: Incremental or bulk filling? *Dental Materials* **24**(**11**) 1501-1505.
3. Knezevic A, Ristic M, Demoli N, Tarle Z, Music S, Negovetic Mandic V (2007) Composite photopolymerization with diode laser *Operative Dentistry* **32**(**3**) 279-284.
4. Bucuta S, Ilie N (2014) Light transmittance and micro-mechanical properties of bulk fill vs. conventional resin based composites *Clinical Oral Investigations* Jan 11 [Epub ahead of print] doi: 10.1007/s00784-013-1177-y.
5. Ivoclar Vivadent (2013) Tetric EvoCeram Bulk Fill Scientific Documentation. Retrieved online February 1, 2014 from: http://www.ivoclarvivadent.com/zoolu-website/media/document/17021/Tetric+EvoCeram+Bulk+Fill.
6. Dentsply (2011) SDR Scientific Compendium. Retrieved online February 1, 2014 from: http://www.dentsplymea.com/sites/default/files/Scientific%20compendium%20SDR%20-%202011.pdf.
7. Czasch P, Ilie N (2013) *In vitro* comparison of mechanical properties and degree of cure of bulk fill composites *Clinical Oral Investigations* **17**(**1**) 227-235.
8. Alrahlah A, Silikas N, Watts DC (2014) Post-cure depth of cure of bulk fill dental resin-composites *Dental Materials* **30**(**2**) 149-154.
9. Fleming GJ, Awan M, Cooper PR, Sloan AJ (2008) The potential of a resin-composite to be cured to a 4 mm depth *Dental Materials* **24**(**4**) 522-529.
10. Moorthy A, Hogg CH, Dowling AH, Grufferty BF, Benetti AR, Fleming GJ (2012) Cuspal deflection and microleakage in premolar teeth restored with bulk-fill flowable resin-based composite base materials *Journal of Dentistry* **40**(**6**) 500-505.
11. Roggendorf MJ, Kramer N, Appelt A, Naumann M, Frankenberger R (2011) Marginal quality of flowable 4-mm base vs. conventionally layered resin composite *Journal of Dentistry* **39**(**10**) 643-647.
12. Leprince JG, Palin WM, Hadis MA, Devaux J, Leloup G (2013) Progress in dimethacrylate-based dental composite technology and curing efficiency *Dental Materials* **29**(**2**) 139-156.
13. Krifka S, Seidenader C, Hiller KA, Schmalz G, Schweikl H (2012) Oxidative stress and cytotoxicity generated by dental composites in human pulp cells *Clinical Oral Investigations* **16**(**1**) 215-224.
14. Lee S, Kim T, Son S, Park J, Kim J, Kim H, Kwon YH (2013) Influence of light-curing units on the polymerization of low-shrinkage composite resins *Dental Materials Journal* **32**(**5**) 688-694.
15. Leprince JG, Leveque P, Nysten B, Gallez B, Devaux J, Leloup G (2012) New insight into the "depth of cure" of dimethacrylate-based dental composites *Dental Materials* **28**(**5**) 512-520.
16. Flury S, Hayoz S, Peutzfeldt A, Husler J, Lussi A (2012) Depth of cure of resin composites: Is the ISO 4049 method suitable for bulk fill materials? *Dental Materials* **28**(**5**) 521-528.
17. Vasudeva G (2009) Monomer systems for dental composites and their future: A review *Journal of the California Dental Association* **37(6)** 389-398.
18. Tarle Z, Knezevic A, Demoli N, Meniga A, Sutalo J, Unterbrink G, Ristic M, Pichler G (2006) Comparison of composite curing parameters: Effects of light source and curing mode on conversion, temperature rise and polymerization shrinkage *Operative Dentistry* **31**(**2**) 219-226.
19. Alshali RZ, Silikas N, Satterthwaite JD (2013) Degree of conversion of bulk-fill compared to conventional resin-composites at two time intervals *Dental Materials* **29**(**9**) e213-217.
20. Bouschlicher M, Rueggeberg F, Wilson B (2004) Correlation of bottom-to-top surface microhardness and conversion ratios for a variety of resin composite compositions *Operative Dentistry* **29(6)** 698-704.
21. Shin WS, Li XF, Schwartz B, Wunder SL, Baran GR (1993) Determination of the degree of cure of dental resins using Raman and FT-Raman spectroscopy *Dental Materials* **9(5)** 317-324.
22. Marovic D, Panduric V, Tarle Z, Ristic M, Sariri K, Demoli N, Klaric E, Jankovic B, Prskalo K (2013) Degree of conversion and microhardness of dental composite resin materials *Journal of Molecular Structure* **1044** 299-302.
23. Pianelli C, Devaux J, Bebelman S, Leloup G (1999) The micro-Raman spectroscopy, a useful tool to determine the degree of conversion of light-activated composite resins *Journal of Biomedical Materials Research* **48(5)** 675-681.
24. Zhang Y, Wang Y (2012) Improved degree of conversion of model self-etching adhesives through their interaction with dentine *Journal of Dentistry* **40**(**1**) 57-63.
25. Leung RL, Fan PL, Johnston WM (1983) Post-irradiation polymerization of visible light-activated composite resin *Journal of Dental Research* **62(3)** 363-365.
26. Mohamad D, Young RJ, Mann AB, Watts DC (2007) Post-polymerization of dental resin composite evaluated with nanoindentation and micro-Raman spectroscopy *Archives of Orofacial Sciences* **2** 26-31.
27. Schneider LF, Consani S, Ogliari F, Correr AB, Sobrinho LC, Sinhoreti MA (2006) Effect of time and polymerization cycle on the degree of conversion of a resin composite *Operative Dentistry* **31**(**4**) 489-495.
28. Burtscher P (1993) Stability of radicals in cured composite materials *Dental Materials* **9(4)** 218-221.
29. Truffier-Boutry D, Demoustier-Champagne S, Devaux J, Biebuyck JJ, Mestdagh M, Larbanois P, Leloup G (2006) A physico-chemical explanation of the post-polymerization shrinkage in dental resins *Dental Materials* **22**(**5**) 405-412.
30. Tarumi H, Imazato S, Ehara A, Kato S, Ebi N, Ebisu S (1999) Post-irradiation polymerization of composites containing bis-GMA and TEGDMA *Dental Materials* **15(4)** 238-242.

31. Halvorson RH, Erickson RL, Davidson CL (2003) The effect of filler and silane content on conversion of resin-based composite *Dental Materials* **19**(**4**) 327-333.

32. Eliades GC, Vougiouklakis GJ, Caputo AA (1987) Degree of double bond conversion in light-cured composites *Dental Materials* **3**(**1**) 19-25.

33. 3M ESPE (2012) Filtek Bulk Fill Technical Product Profile. Retrieved online February 1, 2014 from: http://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSufSevTsZxtUoY_vmx2UevUqevTSevTSevTSeSSSSSS--&fn=Filtek_bulk_fill_flowable_tpp_R2.pdf.

34. Guo G, Fan Y, Zhang JF, Hagan JL, Xu X (2012) Novel dental composites reinforced with zirconia-silica ceramic nanofibers *Dental Materials* **28**(**4**) 360-368.

35. Musanje L, Darvell BW (2006) Curing-light attenuation in filled-resin restorative materials *Dental Materials* **22**(**9**) 804-817.

36. Leprince JG, Palin WM, Hadis MA, Devaux J, Leloup G (2013) Progress in dimethacrylate-based dental composite technology and curing efficiency *Dental Materials* **29**(**2**) 139-156.