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Influence of Spectroscopic Techniques on the Estimation of the Degree of Conversion of Bulk-fill Composites

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Clinical Relevance

Clinicians should understand that degree of conversion (DC) of bulk-fill composites varies between flowable and sculptable materials. The technique of measurement significantly influences the reported values of DC.

SUMMARY

Objectives: To compare the degree of conversion (DC) of different flowable and sculptable bulk-fill composites (BFC), at 0- and 4-mm depths from the surface, by Fourier transform infrared (FTIR), attenuated total reflection FTIR (ATR-FTIR), and FT-Raman spectroscopic techniques.

Methods and Materials: Six BFC were investigated, including three sculptable composites (Admira Fusion [Voco], Aura Bulk Fill [SDI], and X-tra Fill [Voco]) and three flowable composites (Venus Bulk Fill [Heraeus], Filtek [3M], and X-tra Base [Voco]). Three molds of each composite were light cured as specified by the manufacturer. For each mold, slices corresponding to 0-mm (surface) and 4-mm depth were analyzed by spectroscopic techniques: ATR-FTIR, FTIR, and FT-Raman. The spectra of uncured composite material were used as an analytical control for background subtraction of the treated composite. The area and amplitude of the reference peaks (1607 and 1637 cm^{-1}) were obtained to calculate the DC percentage at 0- and 4-mm depth. A Kruskal-Wallis nonparametric test was used for materials, and paired comparisons were made using Mann-Whitney nonparametric test. Wilcoxon's rank test was used for comparison between spectro-

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scopic methods and between 0- and 4-mm depth in each composite. Significance was accepted at $p<0.05$.

Results: FTIR showed significantly lower DC values, both in areas and amplitudes of the peaks, when compared with the results reported by different BFC. Differences between the surface and 4-mm depth were detected more precisely by FT-Raman. ATR-FTIR obtained DC values significantly higher than those obtained by FTIR.

Conclusions: The vibrational spectroscopy method significantly influenced DC measurements of the flowable and sculptable BFC explored.

INTRODUCTION

Composites have become the most commonly used restorative materials in clinical dentistry.[1] A major drawback of resin composites is polymerization shrinkage, which reportedly occurs in the range of 2-5 vol%.[2] Polymerization shrinkage causes stress at the tooth-restoration interface as the elastic modulus of the composite increases during curing. This shrinkage stress is thought to be related to most clinical problems that cause failure of the restorations.[1,3-5]

Bulk-fill composite (BFC) has been introduced to overcome the drawbacks of the rather time-consuming incremental technique. Manufacturers claim that BFCs generate lower polymerization shrinkage stress and have better light transmission properties than conventional composites, which allows them to be used for increments of up to 4- to 5-mm thickness.[5] The capacity for polymerization in depth of BFC has been studied using the scraping test according ISO 4049 specifications,[6,7] microhardness,[6-12] or the degree of conversion (DC).[8,11,13-16] DC is a key material feature of dental resin composites, because it affects both physical and mechanical polymer properties as well as biocompatibility.[17,18] This DC parameter represents the percentage of unreacted carbon double bonds (C=C) in the cured material in relation to the uncured material.[19]

Vibrational spectroscopic techniques, such as Fourier transform infrared (FTIR), attenuated total reflection FTIR (ATR-FTIR), and FT-Raman spectroscopies, have been used to detect and analyze the structural and chemical composition of various materials. Although FT-Raman, FTIR, and ATR-FTIR are complementary spectroscopic techniques, they are dependent on different selection rules and polarization properties. While FTIR spectroscopy is based on the absorption of light, Raman is based on the scattering of light by vibrating molecules (ie, inelastic scattering of vibrating molecules), and ATR-FTIR uses a property of total internal reflection resulting in an evanescent wave. All of these spectroscopic methods are suitable for the analysis of the capacity or polymerization efficiency of dental resins, usually expressed as DC.[16,20,21] Nevertheless, results of DC measurements of dental composites seem to vary for similar materials and technical procedures depending on the sample preparation and the method of spectra analysis: considering overlapped or hidden peaks or the procedure for calculating the amplitude or the areas of the DC reference peaks.[20,22-26] For instance, Pianelli and others[27] found that the DC calculated using the area ratio after deconvolution appeared weaker than that obtained using the height ratio with or without deconvolution. On the other hand, the opposite was found by Khalil and others[26] using FT-Raman spectroscopy.

Many brands are introducing novel BFC in clinical dentistry. Owing to differences in rheological properties and application techniques, BFCs are further classified as either low viscosity (flowable), allowing better adaptation to cavity walls, or high viscosity (sculptable) material types.[17] Although much effort has been made to quantify the DC of bulk composites, the influence of the spectroscopic method used has been scarcely studied. In our study, we compared the polymerization characteristics of the main currently available flowable and sculptable BFC at 0-mm and 4-mm depth curing conditions.

Therefore, the main objectives were to evaluate (1) the influence of the spectroscopy technique (FTIR, ATR-FTIR, and FT-Raman) and the spectrometric analysis method in the calculation of the DC values in BFC and (2) the influence of different types of flowable or sculptable BFC and the curing-depth conditions.

METHODS AND MATERIALS

Sample Preparation

Six BFC were investigated (Table 1), including three flowable (VBF, FBF, and XbBF) and three sculptable (AFBF, ABF, XfBF) composites. Uncured material was inserted into cylindrical stainless-steel molds with an internal hole of 4 mm in diameter and 5 mm height (divided into three parts: 1 mm, 3 mm, and 1 mm; Figure 1).

Table 1: *Bulk-fill Dental Composites Used in the Study*

Material	Code	Shade	Manufacturer	Type	Resin Matrix
Venus Bulk Fill	VBF	Universal	Heraeus Kulzer GmbH, Hanau, Germany	Flowable bulk-fill	UDMA, EBPDMA
Filtek Bulk Fill	FBF	Universal	3 M ESPE, ESPE, St. Paul, MN, USA	Flowable bulk-fill	Bis-GMA, Bis-EMA, UDMA
X-tra Base	XbBF	Universal	Voco GmbH, Cuxhaven, Germany	Flowable bulk-fill	UDMA, Bis-EMA
Admira Fusion	AFBF	A1	Voco GmbH, Cuxhaven, Germany	Sculptable bulk-fill ORMOCER	Aromatic and aliphatic dimethacrylates, methacrylate-functionalized polysiloxane
Aura Bulk Fill	ABF	Universal	SDI Limited Bayswater, Bayswater, Victoria, Australia	Sculptable bulk-fill	UDMA, Bis-EMA, Bis-GMA, TEGDMA
X-tra Fill	XfBF	Universal	Voco GmbH, Cuxhaven, Germany	Sculptable bulk-fill	Bis-GMA, UDMA, TEGDMA

Abbreviations: Bis-EMA, ethoxylated bisphenol-A-dimethacrylate; Bis-GMA, bisphenol-A-glycidyldimethacrylate; EBPDMA, ethoxylated bisphenol A dimethacrylate; TEGDMA, triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate.

The molds were slightly overfilled with the material, and the excess was then extruded, oxygen inhibition prevented and a smooth surface obtained by applying a transparent polyester Mylar strip on the top and bottom of the mold and pressing firmly with a glass slab. Care was taken to minimize entrapped air while uncured materials were placed in the mold. The mold sample was then light cured from the top (ie, in contact with the mold surface, 0-mm depth) as specified by the manufacturer (Table 1), using a light-emitted diode curing unit (1200 mW/cm^2; Bluephase 20i, IvoclarVivadent, Schaan, Liechtenstein). All samples were stored dry at 37°C in

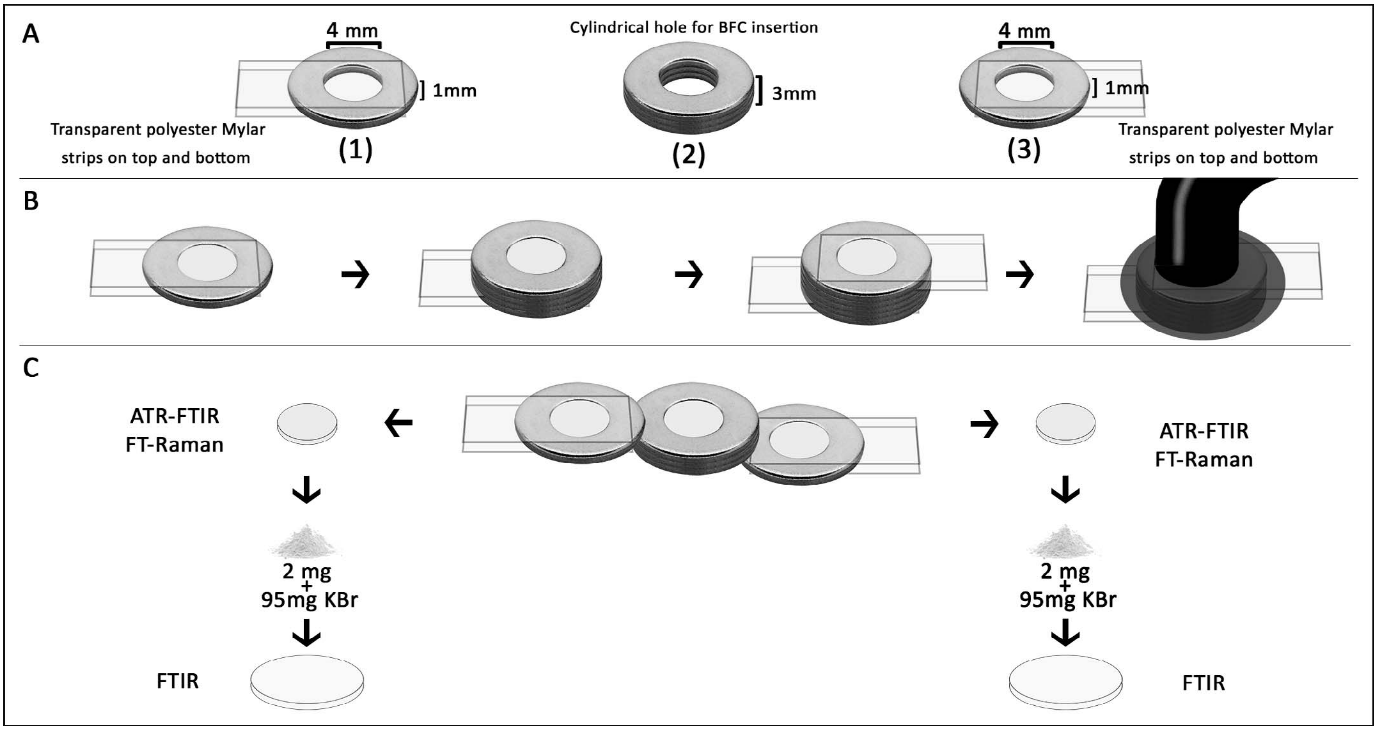

Figure 1. *Sample preparation for Fourier transform infrared (FTIR), attenuated total reflection–Fourier transform infrared (ATR-FTIR), and FT-Raman spectroscopic analyses. (A): Cylindrical stainless-steel mold with an internal hole of 4 mm in diameter and 5 mm in height divided into three parts: (1) and (3) 1-mm thick with transparent polyester Mylar strips at the top and bottom and (2) 3-mm thick. (B): Sequence of placement of the bulk-fill composites and polymerization. (C): After being stored dry at 37°C in the dark for 24 hours, they were unmolded, and two slices (0- and 4-mm depth, left and right, respectively) were obtained and analyzed using ATR-FTIR and FT-Raman. Then, these slices were pulverized, and 2 mg was mixed with 95 mg of potassium bromide to obtain disks under pressure that were analyzed using FTIR. For further details, see the "Methods and Materials" section.*

Table 1: *Bulk-Fill Dental Composites Used in the Study (ext.)*

Material	Filler		Curing Time
	Composition	Load (wt%/vol %)	
Venus Bulk Fill	Ba-Al-F-Silicate glass, YbF_3, SiO_2	65/38	20 s
Filtek Bulk Fill	Ytterbium trifluoride filler (sizes range from 0.1 to 5.0 μm) and zirconia/silica (size range of 0.01 to 3.5 μm)	64.5/42.5	20 s
X-tra base	Barium glass ceramic, fumed silica (size 3.5 μm)	75/60 (58)	10 s
Admira Fusion	Ba-Al-glass, pyrogenic SiO_2	84/-	20 s
Aura Bulk Fill	Silica, silinated barium glass particles, Ultra High Density pre-polymerized filler barium glass particles.	82/65	20 s
X-tra fill	Barium glass ceramic, fumed silica (size 3.5 μm)	86/70.1	10 s

darkness for 24 hours after irradiation prior to further analyses.

Three molds of each BFC were processed, and two slices from each one of these molds, at 0- and 4-mm depth from the surface, were obtained. Accordingly, three samples of each uncured composite material were also analyzed. Three spectra from each sample were recorded using different spectroscopic techniques.

In Vitro Analysis

Fourier transform–Raman spectroscopy (FT-Raman)—Spectra were obtained using a JASCO NRS-5100 spectrometer (Jasco Inc, Easton, MD, USA) coupled to an optical Olympus microscope and equipped with a charge-coupled device detector (1024 × 256 pixels) cooled by a Peltier-effect module. FT-Raman spectra were excited using a 785-nm red diode laser kept at 500 mW. Spectra were acquired between 1500 and 1750 cm^{-1} with a resolution of 1 cm^{-1}, an exposure time of 10 seconds, and 10 accumulations.

ATR-FTIR—Samples were analyzed using an FTIR JASCO 6200 spectrometer equipped with a diamond-tipped ATR accessory (ATR Pro ONE, Jasco). Samples were placed on the ATR crystal holder covering the entire crystal surface. All spectra were acquired between 600 and 4000 cm^{-1}, with a spectral resolution of 2 cm^{-1}, acquisition time of 10 seconds, and 10 accumulations.

FTIR—Each sample was powdered, and 2 mg was mixed with 95 mg of FTIR-grade potassium bromide (KBr) and pressed under a vacuum at 9 metric tons for 10 minutes.

Infrared spectral data were collected on an FTIR spectrometer (JASCO 6200) coupled with a transmission sample holder. The spectra were acquired in the absorption mode between 600 and 4000 cm^{-1}, at 2 cm^{-1} resolution over 1024 scans. A reference disk (97 mg of KBr) was used for background correction every 10 spectra acquisitions.

Spectral Analysis

Spectral analyses were carried out for the calculation of the DC for all the composite materials at 0 and 4 mm of depth. The DC of each composite was calculated by comparing the area and amplitude of particular peaks in the spectra derived from the uncured and cured resin.

After using a standard baseline technique,[24] a region of the spectra between 1575 and 1660 cm^{-1} was selected, and two peaks were considered for DC calculation (Figure 2): 1607 cm^{-1} (internal standard aromatic carbon double bond, C=C) and 1637 cm^{-1} (methacrylate C=C). For AFBF, based on Ormocer technology, reference peaks were considered at 1584 cm^{-1} (C=C) and at 1638 cm^{-1} (methacrylate C=C). The DC was calculated as follows:

$$\%\mathrm{DC}_{area/amplitude} = \left[1 - \frac{(1637\ \mathrm{cm}^{-1}/1607\ \mathrm{cm}^{-1})_{after\ curing}}{(1637\ \mathrm{cm}^{-1}/1607\ \mathrm{cm}^{-1})_{before\ curing}}\right] \times 100$$

Overlapping peaks were resolved, and their amplitudes and integrated areas were measured using curve-fitting software (Peakfit v4.12, Systat Software, Chicago, IL, USA). The second derivative method was used to resolve the peak calculations within the spectral region. Peak amplitude and position were allowed to vary within 5% and ±2 cm^{-1}, respectively. The degree of smoothing was set at 10% (Savitzky-Golay algorithm), and a mixed Gaussian-Lorentzian function was used to fit the contours (ie, curve shape and width) of the bands, allowing for a detailed and quantitative analysis of

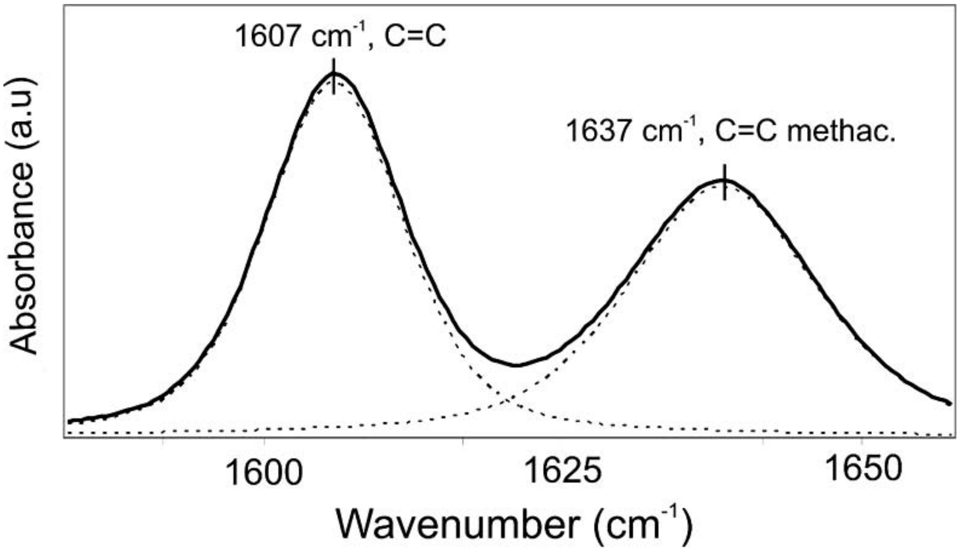

Figure 2. *Curve-fitting analysis for an average FT-Raman spectrum from bulk-fill composites (except for AFBF). Area and amplitude for the two reference peaks were calculated: 1607 cm^{-1} (internal standard aromatic carbon double bond, C=C) and 1637 cm^{-1} (methacrylate C=C).*

DC values. Curve fitting was accepted when r^2 reached values up to 0.995.

Statistical Analysis

After exploring the data distribution (Shapiro-Wilk test), nonparametric statistics were applied. A Kruskal-Wallis nonparametric test was used for these materials, and subsequent paired comparisons were made using a Mann-Whitney nonparametric test. Wilcoxon's rank test was used for comparisons between different spectroscopic methods and between 0- and 4-mm depths in each composite. Significance was accepted at $p<0.05$.

RESULTS

Comparisons Between Vibrational Spectroscopy Methods

Table 2 summarizes the DC measurements by FT-Raman, ATR-FTIR, and FTIR on the surface (0 mm) and at 4-mm depth for the six bulk-fill dental composites analyzed.

When the ratio of the integrated areas was used to determine the DC at 24 hours postcure, ATR-FTIR obtained higher percentages of conversion than the other vibrational spectroscopy methods, although the results for each composite were highly variable.

In the following section, "=" means "not significant" and "<" and ">" mean "significantly lower" and "significantly higher," respectively. At 0-mm depth for flowable BFC, the DC values obtained for VBF by integrated areas were ATR-FTIR=FT-Raman>FTIR, the DC values of FBF were ATR-FTIR>FT-Raman>FTIR ($p<0.012$ for all comparisons), and the DC values of XbBF were ATR-FTIR=FTIR>FT-Raman. ATR-FTIR also gave the highest DC values for the three sculptable BFC, although the DC for AFBF was ranked ATR-FTIR>FT-Raman>FTIR ($p<0.030$); for ABF, the DC was ATR-FTIR>FT-Raman=FTIR; and for XfBF, the DC ranged from 84% to 47%, with the ranking ATR-FTIR>FT-Raman>FTIR ($p<0.020$).

At 4-mm depth, among flowable BFC, VBF and FBF showed similar behavior to that obtained at 0-mm depth. The exception was XbBF, for which ATR-FTIR=FT-Raman>FTIR ($p<0.015$). The highest DC was also obtained with ATR-FTIR for the three sculptable BFC, with similar relations between methods as those described at 0-mm depth, except for AFBF, which showed a DC with ATR-FTIR>FTIR>FT-Raman ($p<0.030$).

When the relation between the amplitude of the reference peaks was considered (Table 2), the DC values for the flowable BFC were highly material dependent at 0-mm depth, VBF obtained a higher DC with FT-Raman compared with ATR-FTIR=FTIR, FBF showed significantly ($p=0.008$) higher DC values for FT-Raman=ATR-FTIR compared with FTIR, and XbBF showed a higher DC by ATR-FTIR>FT-Raman=FTIR. Among the sculptable BFC, ABF and XfBF showed similar DC using ATR-FTIR and FT-Raman, and these values were higher than FTIR values, although the differences were significant only for ABF ($p=0.008$). AFBF achieved similar results with the three spectroscopic methods, at between 55.10% and 56.56%, with no significant differences ($p>0.600$).

Table 2: *Degree of Conversion Values (Mean [SD]) Obtained for Relative Area or Amplitude by FT-Raman, ATR-FTIR, and FTIR at Surface (0 mm) and 4-mm Depth for Six Bulk-fill Dental Composites (BFC)*[a]

	Flowable BFC			**Sculptable BFC**		
	VBF	**FBF**	**XbBF**	**AFBF**	**ABF**	**XfBF**
0 mm						
Area						
FT-Raman	65.21 (2.82)^{2,a}	60.36 (1.67)^{3,a}	50.27 (8.25)^{4,a}	68.80 (8.20)^{1,a}	54.04 (7.31)^{3,4,a}	65.57 (5.71)^{1,2,a}
ATR-FTIR	67.37 (7.78)^{3,a}	71.54 (6.56)^{2,3,b}	68.19 (6.29)^{2,3,b}	76.43 (7.46)^{1,2,b}	81.79 (5.27)^{1,b}	84.07 (3.22)^{1,b}
FTIR	59.46 (5.07)^{1,b}	46.63 (7.96)^{3,c}	59.55 (7.63)^{2,b}	56.61 (6.18)^{1,c}	54.33 (7.02)^{1,2,a}	47.32 (9.16)^{2,3,c}
Amplitude						
FT-Raman	73.01 (2,01)^{1,A}	63.13 (1.59)^{2,A}	54.34 (3.08)^{3,A}	56.56 (10.38)^{2,3,A}	57.06 (6.83)^{2,3,A}	58.12 (3.87)^{3,A}
ATR-FTIR	65.16 (7.26)^{1,B}	58.76 (6.35)^{1,2,A}	59.51 (4.20)^{2,3,B}	56.15 (9.43)^{3,A}	65.69 (10.80)^{1,2,3,A}	63.75 (4.23)^{1,2,A}
FTIR	60.41 (3.87)^{1,B}	47.79 (3.76)^{2,B}	49.83 (6.27)^{2,A}	55.10 (7.40)^{1,2,A}	43.95 (3.17)^{3,B}	46.05 (6.96)^{2,3,B}
4 mm						
Area						
FT-Raman	73.95 (7.21)^{1,a}	62.65 (2.86)^{2,a}	58.72 (2.47)^{3,a}	50.79 (7.33)^{2,3,a}	48.83 (4.77)^{2,3,a}	57.20 (8.32)^{2,3,4,a}
ATR-FTIR	78.73 (9.50)^{1,a}	71.97 (5.47)^{3,b}	56.09 (8.46)^{3,a}	74.44 (8.59)^{1,2,b}	80.62 (5.97)^{1,b}	79.70 (5.37)^{1,b}
FTIR	55.87 (4.63)^{1,b}	41.64 (5.97)^{3,c}	48.91 (3.88)^{2,b}	61.37 (7.91)^{1,c}	56.51 (6.87)^{1,c}	48.77 (5.84)^{2,c}
Amplitude						
FT-Raman	75.53 (1.38)^{1,A}	65.51 (1.77)^{2,A}	60.01 (1.56)^{3,A}	44.01 (8.01)^{5,A}	52.20 (4.46)^{4,A}	52.21 (4.26)^{4,A}
ATR-FTIR	76.79 (7.27)^{1,A}	66.09 (8.65)^{2,A}	52.94 (4.25)^{4,B}	58.95 (6.51)^{3,B}	67.57 (8.86)^{1,2,B}	62.04 (2.83)^{2,3,B}
FTIR	56.21 (3.40)^{2,B}	43.44 (6.23)^{3,B}	46.73 (4.98)^{3,C}	60.78 (4.47)^{1,B}	44.20 (5.40)^{3,C}	45.50 (5.35)^{3,C}

[a] *Different numbers in rows represent significant differences between materials. They are ordered from greater to lower values. Different lowercase letters in columns represent significant differences in the comparison between techniques, in the area relation, for each BFC. Different uppercase letters in columns represent significant differences in the comparison between techniques, in the amplitude relation, for each BFC.*

At 4-mm depth, VBF and FBF showed similar DC using FT-Raman and ATR-FTIR, while FTIR obtained significantly lower DC values ($p<0.008$ in all comparisons). DC values for XbBF were ranked FT-Raman>ATR-FTIR>FTIR ($p<0.030$). Among the sculptable materials, ABF and XfBF had the highest DC values using ATR-FTIR>FT-Raman>FTIR ($p<0.040$), while for AFBF, the methods were ranked FTIR=ATR-FTIR>FT-Raman.

Comparisons Between Methods of Analysis: Relation of Integrated Areas vs Amplitude of Reference Peaks

Figure 3 summarizes the differences between the mean DC calculated for each BFC with relation to areas or amplitudes of the reference peaks, at 0- and 4-mm depth. Using ATR-FTIR, at 0-mm depth, all the BFC behaved better when the relation of areas was applied, except VBF, which had a similar DC using both methods of analysis. At 4-mm depth, only sculptable BFC had a significantly higher DC by areas ratio, with differences in DC with respect to amplitudes ratio next to 20% for XfBF. With FT-Raman, we obtained higher DC values using the relation of amplitudes for flowable BFC. Differences were significant for VBF and FBF at 0-mm depth ($p=0.008$ in both materials) and for FBF only at 4-mm depth ($p=0.008$). Sculptable composites AFBF and XfBF had higher DC values (about 12% and 7%, respectively) using the relation of areas rather than amplitudes at 0-mm depth ($p=0.008$) and at 4-mm depth differences were about 14% for AFBF ($p=0.008$) and 5% for XfBF ($p=0.139$); ABF demonstrated the opposite results, with significantly higher DC values (about 3%-4%, $p=0.008$) using the amplitudes ratio. Finally, by FTIR, no significant differences were found between the DC using areas or amplitudes ratios, except for XbBF at 0-mm depth ($p=0.021$) and ABF at 0- and 4-mm depth ($p=0.008$ both).

Comparisons Between BFC Materials

When we compared the relative efficiency of cure, the impact of the vibrational spectroscopy technique and the methodology for spectral analysis were evident, along with that of material. Significant differences are represented by different numbers within rows in Table 2 and are ordered from higher to lower values. At 4-mm depth, flowable BFC had a better DC than sculptable BFC using FT-Raman spectroscopy, but using ATR-FTIR, ABF, and XfBF (two sculptable BFC) achieved the best results. At 4-

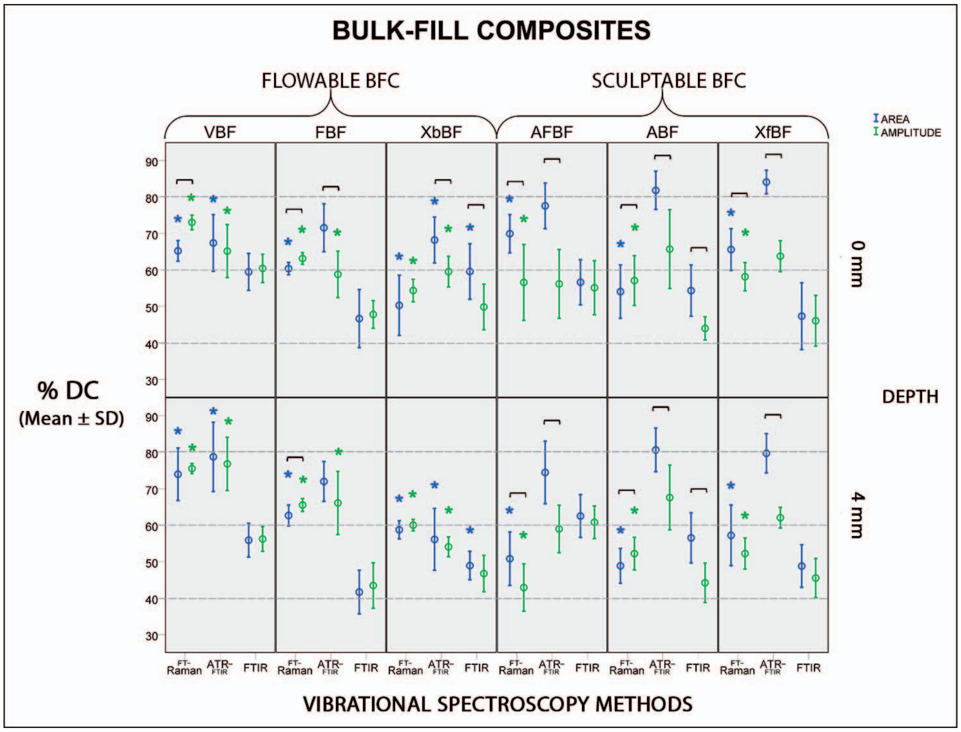

Figure 3. *Degree of conversion values (mean ± SD) obtained for relative area (blue lines and boxes) or amplitude (green lines and boxes) by FT-Raman, attenuated total reflection–Fourier transform infrared, and Fourier transform infrared at the surface (0 mm) and 4-mm depth for six bulk-fill dental composites. Square bracket indicates statistically significant differences between area and amplitude. Asterisk (*) indicates significant differences between 0 and 4 mm for area and amplitude separately, in each technique.*

mm depth, XbBF showed a drop in DC with respect to that obtained at 0-mm depth, in FTIR using areas and amplitudes relations. At 4-mm depth, VBF gave the most consistent results, with DC ranging from 73% to 78% using FT-Raman and ATR-FTIR and more than 55% by FTIR.

Comparison as a Function of Depth

It was not possible to identify a homogenous trend in the function of depth for all BFC, nor for flowable or sculptable composites as a group, for all vibrational spectroscopic methods. When considering both methods of analysis (ratio of areas and ratio of amplitudes; Figure 3), sculptable BFC did not show any differences in DC values between 0- and 4-mm depth by FTIR or ATR-FTIR. However, FT-Raman spectroscopy showed a significant reduction in the DC at 4 mm with respect to the surface. Flowable BFC showed the opposite behavior, with an increase in the DC at 4-mm depth with respect to the surface by FT-Raman spectroscopy, and for VBF, this increase was also detected by ATR-FTIR. XbBF was an exception, showing a drop in DC at 4 mm with respect to 0 mm in ATR-FTIR and FTIR.

DISCUSSION

This study analyzed the influence of spectroscopic technique (FTIR, ATR-FTIR, and FT-Raman) and the method of spectral analysis on the estimation of the DC for six bulk-fill (flowable and sculptable) composites. The results revealed that the BFC had significant differences in their DC values depending on the vibrational spectroscopy technique used and as a function of the method of spectral analysis (ie, the calculation of integrated areas or the amplitude of the reference peaks). Differences in nominal mean DC values were detected for selected materials, calculated at 0- and 4-mm depth with respect to the surface, and in comparisons between materials, depending on the spectroscopic technique and the method of spectral analysis.

Other factors influencing the DC measurements and related to the experimental conditions were controlled in our study, such as the distance of the light guide to the specimen surface,[28,29] which was set at 0 mm, and light curing from the top in contact with a transparent polyester Mylar strip. A plastic film on the top and bottom of the mold of the specimens was used because it minimizes light attenuation[28] and provides a smooth surface for FT-Raman analysis. Although the impact of such attenuation on the DC was not considered in the present study, the real DC values of the BFC would not be lower than those estimated. Temperature during manipulation has been shown to increase the DC of some BFC.[17] In the present study, the manipulation was performed at laboratory temperature (22°C) and specimens were stored at 37°C in darkness for 24 hours after irradiation.[14,16,30] Although each compound has its own polymerization kinetics, after 24 hours, polymerization should be considered sufficient when using the curing time recommended by the manufacturers.[8,14,16] The thickness of the specimens is also known to impact the DC features of composites.[31] We used 4- to 5-mm-thick specimens because BFC are designed to be suitable for placement in such increments, and we also considered this thickness to be clinically relevant.[14,18,32]

Methodological standardization for spectral analyses is crucial for comparison between quantitative measurements in material characterization. In the present study, we performed detailed spectroscopic analyses of different molecular constituents in several composite resins. We employed a specific procedure during data acquisition and spectral analyses by FTIR, ATR-FTIR, and FT-Raman spectroscopies, using identical spectrometric methodology to avoid possible analytical data deviation due to the analytical procedure. The area and amplitude ratios between the two main reference peaks (C=C absorption bands at 1607 cm^{-1} and 1637 cm^{-1}) were used to determine the DC of dental resins.[24] The only exception was applied to the AFBF composite, an Ormocer-based sculptable composite, which consists of large and precondensed molecules of an inorganic matrix with a high degree of cross-linking.[33] In this case, the peak position at 1588 ± 4 cm^{-1} was considered as the reference peak, as proposed by several authors using different vibrational spectroscopic analyses.[34] These reference peaks were resolved by a second derivative methodology and fitted to a mixed Gaussian-Lorentzian function for detailed quantitative measurements. This spectrometric method was used by Gauthiers and others[25] on a mix of polymers and demonstrated the best correlation with the molar ratio of monomers in several calibration mixes using FTIR techniques.

In the present study, the use of area or amplitude to calculate DC had a different impact depending on whether FT-Raman or infrared methods (FTIR and ATR-FTIR) were applied. FT-Raman rendered higher mean DC values using the relative amplitude of the peaks rather than the area for flowable BFC; the opposite was found for sculptable BFC. In general, infrared methods produced higher DC values using the area rather than the amplitude relations. Rueggeberg and others[24] concluded that when using an appropriate method of subtraction of the baseline, no significant differences in DC were obtained between the ratio of amplitudes or areas of the peaks. This standard baseline method is well suited for FT-Raman spectroscopy.[25,27,35] Nevertheless, Khalil and others,[26] who also used FT-Raman spectroscopy, obtained higher DC values using the ratio of the areas. The most obvious impact of the spectroscopy technique applied was the finding of different behaviors of the DC at 4 mm with respect to the surface (ie, 0-mm depth) for flowable and sculptable BFC depending on whether the FT-Raman or IR techniques (FTIR and ATR-FTIR) were used. Flowable BFC had significantly higher DC values at 4-mm depth when determined by FT-Raman, and the opposite was found for high-density (sculptable) BFC, that is, a significant drop in their DC at 4 mm with respect to that obtained at 0 mm. The different DC values observed in some other studies based on sample specimen preparation,[32] storage,[18] or spectroscopy method[16] make it difficult to compare their results with the present study.

ATR-FTIR is the method most often used to study the DC of BFC. We observed a significant increase in the DC for VBF and a nonsignificant increase for FBF at depth (4 mm) with respect to the surface (0 mm) when using FT-Raman and ATR-FTIR measurements, while FTIR analyses underestimated DC values at depth. XbBF showed the opposite results with a fall in the DC at 4-mm depth with respect to the surface using ATR-FTIR. Similar results were reported by Zorzin and others,[11] with DC values of 65.24% at the surface and 62.53% at 4 mm. Czasch and Ilie[8] reported a DC of 64.9% at 0.1 mm and a slightly higher DC at 4-mm depth (66.1%) for VBF 5 minutes after curing. Marovic and others[15] attributed the increase in DC at depth with respect to the surface to heat formation due to the exothermic nature of free radical bulk polymerization, which gave rise to an increase in the DC in deeper parts of a bulky specimen, mainly in composites with a lower filler content. This could explain the differences in behavior between VBF with 65 wt% filler (38 vol%) and XbBF with 75 wt% (58 vol%). An increase in filler content reduces the DC.[34] Interestingly, regular composites that presented high light transmission showed no correlation between thickness and DC.[36,37] Among the BFC included in the present study, XfBF is the most studied sculptable BFC. The DC of XfBF varies from 70%[17] to 47.25%[38] at the surface. Using FTIR, Tarle and others[12] observed an increase from 72% at 1-mm depth to 73.9% at 4-mm depth, and these values were higher than the DC values found in the present study.

From a clinical point of view, DC is an important factor to consider when choosing a restorative material. According to other authors, the DC of the BFC used in the current study is strongly material dependent.*

Focusing on individual materials, it is difficult to determine the possible interactions between composition and method of spectroscopy and analysis in the DC of BFC. There is no consensus on the minimal %DC requirements for the main restorative materials currently in use. However, it has been postulated that a conversion of at least 55% is desirable for occlusal layers.[38,40] In our study, if FTIR was applied as the spectroscopic technique to calculate DC, only three BFC would be clinically acceptable. In this case, it should also be taken into account that the state of aggregation of the BFC (powdered samples) as well as the absorption mode analyses for the FTIR technique may also influence the spectrometric measurements of DC values. Using FT-Raman, the DC of sculptable BFC at 4-mm depth ranged from 48% to 57%, making them unsuitable for clinical application, while the ATR-FTIR peak area ratio results would make them highly recommendable, with DC values ranging from 74% to 80%. It is interesting to note that the differing chemistry of the monomeric resin formulations and filler characteristics (type of volume fraction, density, and particle size and distribution) contribute to significant differences in the DC between restorative composites.[37] The DC of different monomer systems decreases in the following order: triethylene glycol dimethacrylate>urethane dimethacrylate (UDMA)>ethoxylated bisphenol-A-dimethacrylate (Bis-EMA)>bisphenol-A-glycidyldimethacrylate (Bis-GMA).[41] The DC is mainly related to the glass transition temperature (T_g) of the unreacted monomer.[41,42] Nevertheless, differences in T_g between conventional composites and BFC were only small in previous studies.[43,44]

In current BFC technology, two approaches have been adopted to manage high in-depth conversion: the first is by increasing translucency[11] by increasing filler size and matching the refractive index of the filler and resin matrix.[45] The second way is by enhancing curing by adding or combining new photoinitiators, for example, alpha diketone initiators such as camphorquinone, phenylpropanedione, and acylphosphine oxide and germanium-based compounds such as bis-(4-methoxybenzoyl)diethylgermane, which can be irradiated using visible light.[38,46] The light absorption characteristics of the photoinitiators were associated with polymerization and thus could influence the DC and be used as parameters for determining the polymerization efficiency of BFC.[47] The manufacturers of the BFC included in this study did not report the inclusion of such photoinitiators in their brochures or safety data sheets. In the current study, VBF obtained the most consistent results, with DC at 4-mm depth ranging from 73% to 78% using FT-Raman and ATR-FTIR analyses and from 55.87% to 56.21% by FTIR for the area and amplitude ratios, respectively. This high DC is consistent with previous reports[13,15,28] and could be explained by the relatively low filler load (38 vol%), very high translucency,[16] and the absence of Bis-GMA in VBF. Experimental composites containing UDMA had, on average, 1.2 and 1.3 times higher conversion at 1- and 4-mm depth, respectively, than those containing Bis-GMA, as well as improved handling properties.[48] FBF has a more complex monomer composition (see Table 1 for resin matrix composition). The DC of FBF was found to significantly decrease at 4-mm depth, which was attributed to the Zr present in the filler, as this has been shown to decrease translucency due to resin/filler refractive index mismatch.[16,28] The content of 50-60 wt% of silane-treated ceramic filler could also account for the lower DC.[34] In the opinion of Alshali and others,[13] the low DC found 24 hours after curing for XbBF (62%) and FBF (50%) was related to the presence of Bis-EMA in their monomer composition. The stiff central phenyl ring core of this monomer can significantly restrict the mobility of UDMA monomers and decrease their reactivity and ultimate conversion value. In our opinion, the lower irradiance of the specimens (600 mW/cm^2) in the study of Alshali and others[13] could also partially explain the lower values found in their study with respect to the present study. The sculptable BFC included in our study are composed of 84 wt% (AFBF) and 85 wt% (XfBF) filler. XfBF demonstrated excellent light transmission through 6-mm specimens, which can be attributed to the increased filler size and potentially improved matching between the refractive indices of filler particles and the resin matrix.[12] A DC of 73.9% was reported by Tauböck and others[17] for XfBF at 4-mm depth using slight experimental modifications and FTIR analyses. In the present study, the DC values of XfBF at 4-mm depth ranged from 79.70% using ATR-FTIR and the area ratios to 45.50% using the FTIR intensities ratio.

In summary, the results of this study reveal the impact of the spectroscopic technique and spectral methodology for calculation of the DC values of BFC materials. Based on our findings, the hypothesis of

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[*] *References 8, 12, 14, 15, 17, 28, 29, 36, 39.*

equality between FT-Raman and IR spectroscopic techniques and spectrometric analysis to calculate the DC must be rejected. The use of a standard methodology of analysis revealed relevant differences between the DC values obtained for the current BFC. Overall, this study provides a complete analytical data set based on different spectroscopic methods to evaluate the features of DC materials at depth for flowable and sculptable composites. The differences obtained indicate that the information on DC should be considered with caution when selecting BFC restorative materials in the clinic.

CONCLUSIONS

The spectroscopic technique (FT-Raman, ATR-FTIR, and FTIR) influences DC measurements of BFC materials, with higher DC values in most cases for ATR-FTIR calculations. The spectrometric methodology (ie, using peak area or amplitude estimation) causes significant variations in DC values depending on the vibrational technique used. The DC also differed significantly among flowable and sculptable composites. Furthermore, the DC showed different behaviors according to depth, with higher values for flowable composites at 4 mm and for sculptable composites at the surface.

The observed differences mean that information on DC should be considered with caution when selecting BFC restorative materials. This information should also be considered when evaluating the DC features associated with different dental resin composites in the clinic (ie, composition, mechanical, biocompatibility properties).

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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