

Discrepancies in degree of conversion measurements by FTIR

Fabrício Mezzomo Collares
Fernando Freitas Portella
Vicente Castelo Branco Leitune
Susana Maria Werner Samuel

Dental Materials Laboratory, School of Dentistry, Universidade Federal do Rio Grande do Sul - UFRGS, Porto Alegre, RS, Brazil.

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Corresponding Author:

Fabrício Mezzomo Collares
E-mail: fabricao.collares@ufrgs.br

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Abstract: The purpose of this study was to evaluate the influence of the internal standard peak on the measured degree of conversion (DC) for methacrylate-based resins analyzed by Fourier-transform infrared spectroscopy (FTIR). The influence of different baseline measurement methods was also determined. Different blends were prepared, mixing BisGMA/BisEMA and BisGMA/TEGDMA at proportions of 0% to 100%, in weight. Camphoroquinone and ethyl-4-dimethylamino-benzoate were used to permit the light activation of blends. Degree of conversion was evaluated using FTIR equipped with an attenuated total reflectance (ATR) device. Samples were dispensed onto ATR crystal and light activated for 40 s. The DC was calculated by relating the height of the peak 1637 cm^{-1} to the intensity of different internal standard peaks (1715 , 1608 , or 1582 cm^{-1}), measured using two different baseline methods, before and after polymerization. Data were compared by ANOVA at 5% significance. The relationship between DC and monomer ratio was obtained by regression analysis. Double-bond conversion ranged from 32.75% to 78.50% for BisGMA/BisEMA blends, and from 32.75% to 76.22% for BisGMA/TEGDMA blends. For the BisGMA/BisEMA blends, the DC showed a linear association with the composition of the comonomer blends, independent of the internal standard peak and baseline method used. In contrast, the trends in DC for BisGMA/TEGDMA blends were different for each method of measurement. The internal standard peaks and measurement baseline should be taken into account when using FTIR to calculate the DC of methacrylate-based resins, especially comonomer blends containing a high degree of monomers that lack aromatic rings.

Descriptors: Polymerization; Bisphenol A-Glycidyl Methacrylate; Dental Materials.

Introduction

The degree of conversion (DC) of polymerizable resins has been widely investigated in the dental literature.¹⁻⁵ A high degree of double-bond conversion of methacrylate-based resins yields favorable mechanical properties^{6,7} and reduced degradation of the polymer.⁶ Despite the high DC achieved in dental resins, complete conversion of aliphatic carbon-carbon double bonds is typically not achieved. The unconverted double bonds remaining in the resin arise from at least two situations, namely, unreacted monomers or pendant double bonds at the extremities of polymer chains.

Unreacted monomers in the polymer network may irritate surrounding tissues.⁸⁻¹⁰ Furthermore, low DC may render the polymer more prone to oxidation and hydrolytic degradation over time,⁶ decreasing the success of restorative procedures.

One of the most common methods to determine the extent of double-bond conversion is Fourier-transform infrared spectroscopy (FTIR),^{2,11} which can detect the stretching vibrations of carbon-carbon double bonds involved in polymerization.¹¹ The method typically utilizes the height ratio of the peaks corresponding to aliphatic (1640 cm^{-1}) and aromatic (1610 cm^{-1}) double bonds² to determine the DC. However, not all dental methacrylate-based polymers contain aromatic rings. Moreover, currently available dental polymer blends present different monomer compositions compared to each other (i.e., BisGMA, TEGDMA, BisEMA and UDMA) and ratios.¹²⁻¹⁵ Because FTIR measurements of DC use the aromatic carbon-carbon double bond peak as internal standard, variations in comonomer blend composition and ratio can influence the results. FTIR spectra of methacrylate-based dental materials also present other peaks related to carbon bond stretching, at 1715 and 1580 cm^{-1} . Therefore, it is of great interest to investigate whether these peaks may be used as internal standards in FTIR to determine the DC.

The purpose of this study was to evaluate the influence of the internal standard peak on the measured degree of conversion (DC) for methacrylate-based resins analyzed by FTIR. Two statistical null hypotheses were tested:

1. that modifying the internal standards does not influence the DC of comonomer blends, and
2. that the baseline used to measure the peak height does not influence the DC results.

Methodology

Materials

Bisphenol-A glycol dimethacrylate (BisGMA) was blended with monomers of either ethoxylated bisphenol-A glycol dimethacrylate 6 (BisEMA) or triethylene glycol dimethacrylate (TEGDMA). Concentrations of BisEMA and TEGDMA in BisGMA were varied from 0% to 100% by weight. To each sample was added 1% mol of camphoroquinone, as

a photosensitizer, and 1% mol of ethyl-4-dimethylamino-benzoate, as a reducing agent. All reagents were obtained from Esstech Inc., Essington, USA.

Degree of conversion analysis

The DC was evaluated by FTIR (Vertex 70, Bruker Optics, Ettlingen, Germany). The spectrometer was coupled to a horizontal attenuated total reflectance (ATR) device consisting of a diamond crystal of 2 mm in diameter (Platinum ATR-QL, Bruker Optics, Ettlingen, Germany). A mid-infrared detector (MIR ATR A225 Diamont, Bruker Optics, Ettlingen, Germany) was used to capture the reflected IR. A support device was used to affix the light-curing unit at a distance of 5 mm from the sample. A drop of each sample ($n = 3$), more than 1 mm thick and sufficiently wide to cover the entire surface of the diamond crystal, was directly dispensed onto the ATR crystal and photoactivated for 40 s by a light-emitting diode (Radii, SDI, Bayswater, Australia). The irradiance value was 1200 mW/cm^2 , confirmed with a digital power meter (Ophir Optronics, North Andover, USA). Sixteen co-addition scans were made at 10 kHz velocity and 4 cm^{-1} resolution, with an instrument aperture of 6 mm. Absorbance spectra were obtained before and immediately after light polymerization using Opus software (Opus 6.5, Bruker Optics, Ettlingen, Germany), with Blackman-Harris 3-Term apodization over the range of 4000 to 400 cm^{-1} . Spectra were transferred to IrfanView 4.25 software (Irfan Skiljan, Wiener Neustadt, Austria), and different baselines were traced onto them, according to Figure 1. The peak height was measured from the top of the peak to the baseline.

The DC for each blend, polymerized and unpolymerized, was determined by the ratio of the absorbance peak corresponding to the aliphatic carbon-carbon double bond (1637 cm^{-1} peak height) with that of the internal standard (1715 , 1608 , and 1582 cm^{-1} peak height), according to methods described in a previous study.¹¹

Statistical analysis

The DC data of each comonomer blend was analyzed by one-way ANOVA (internal standard) and *post-hoc* Tukey test. The relationship between DC

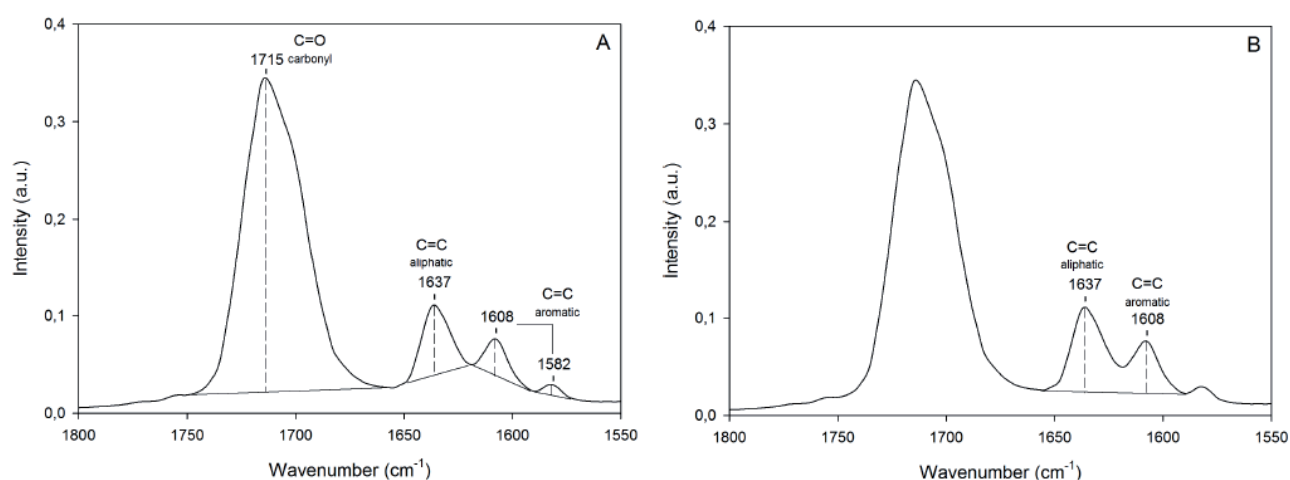


Figure 1 - Schematic representation of the baseline methods proposed to determine the ratios of the absorbance peaks corresponding to aliphatic (1637 cm^{-1}), aromatic (1608 and 1582 cm^{-1}) or carbonyl (1715 cm^{-1}) bonds. The peak heights were measured in relation to the baseline, determined as follows. **(A)** Baseline was traced by connecting the troughs of each peak. **(B)** Baseline was obtained by connecting the 1637 cm^{-1} initial trough and the 1608 cm^{-1} final trough.

Table 1 - Mean (standard deviation) DC (%) for BisGMA/BisEMA blends, measured using different internal standard peaks.

BisGMA/ BisEMA ratio	Internal standard			
	1715 cm^{-1}	$1608\text{ cm}^{-1\text{a}}$	$1608\text{ cm}^{-1\text{b}}$	1582 cm^{-1}
0/100	68.68 (1.43) ^b	77.88 (1.24) ^a	71.31 (0.93) ^b	78.50 (1.98) ^a
10/90	68.76 (0.82) ^b	78.07 (0.78) ^a	67.35 (0.86) ^b	78.03 (1.24) ^a
20/80	61.46 (1.59) ^c	72.28 (1.31) ^a	65.89 (0.83) ^{bc}	70.06 (3.25) ^{ab}
30/70	53.85 (2.10) ^c	66.41 (1.87) ^a	59.75 (2.39) ^{bc}	62.97 (3.03) ^{ab}
40/60	54.53 (1.06) ^c	65.83 (0.40) ^a	59.09 (1.42) ^b	63.56 (1.84) ^a
50/50	51.08 (1.15) ^c	62.21 (0.73) ^a	56.50 (0.82) ^b	60.34 (2.56) ^{ab}
60/40	49.88 (0.83) ^c	61.01 (0.06) ^a	54.61 (0.45) ^b	60.63 (0.57) ^a
70/30	45.28 (2.36) ^b	54.45 (2.09) ^a	46.59 (1.50) ^b	55.89 (2.93) ^a
80/20	43.29 (0.13) ^c	53.79 (0.27) ^a	48.29 (2.30) ^b	53.70 (1.49) ^a
90/10	34.14 (1.46) ^b	43.91 (2.02) ^a	41.37 (0.26) ^a	40.67 (3.07) ^a
100/0	32.75 (1.58) ^b	40.02 (2.32) ^a	33.99 (3.26) ^{ab}	38.14 (3.49) ^{ab}

Means followed by distinct letters in the same line are significantly different ($p < 0.05$).

and comonomer blend ratio or internal standard was analyzed by linear regression, yielding a correlation of determination (R^2). All analyses were conducted at a statistical significance level of 5%.

Results

Tables 1 and 2 show the DC of the polymer blends, measured by different methods. The baseline tracing (Figure 1) influenced the reported DC, as illustrated in Figures 1A and 1B, where the height measurement of the 1608 cm^{-1} internal stan-

dard peak was performed according to two different baseline tracing methods ($1608\text{ cm}^{-1\text{a}}$ and $1608\text{ cm}^{-1\text{b}}$). Double-bond conversion ranged from 32.75% to 78.50% for BisGMA/BisEMA blends, and from 32.75% to 76.22% for BisGMA/TEGDMA blends. Use of $1608\text{ cm}^{-1\text{a}}$ as an internal standard yielded the highest reported values of DC for almost all analyses.

BisGMA/BisEMA blends

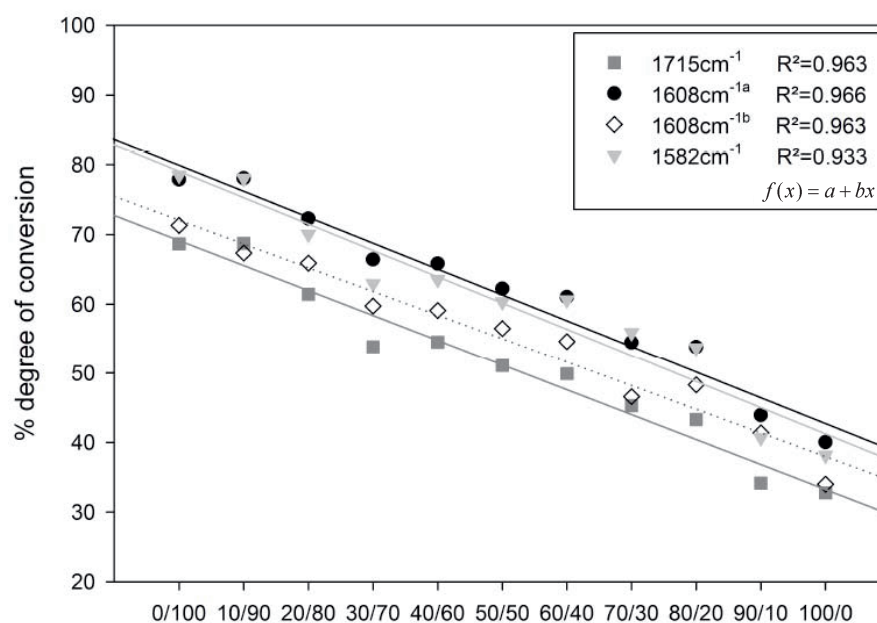
Trends in DC for BisGMA/BisEMA blends were

Table 2 - Mean (standard deviation) DC (%) for BisGMA/TEGDMA blends, measured using different internal standard peaks.

BisGMA/TEGDMA ratio	Internal standard			
	1715 cm ⁻¹	1608 cm ^{-1a}	1608 cm ^{-1b}	1582 cm ⁻¹
0/100	38.83 (4.62) ^a	*	40.19 (6.68) ^a	*
10/90	50.43 (0.66) ^b	76.22 (2.31) ^a	50.96 (0.33) ^b	*
20/80	53.12 (0.66) ^b	73.63 (1.52) ^a	53.68 (0.48) ^b	55.44 (14.01) ^{ab}
30/70	53.63 (0.95) ^b	70.12 (1.73) ^a	56.40 (0.67) ^b	58.63 (4.70) ^b
40/60	54.92 (1.22) ^b	70.93 (0.91) ^a	58.83 (0.57) ^b	65.92 (3.86) ^a
50/50	55.52 (0.72) ^c	68.31 (1.08) ^a	59.98 (0.47) ^b	67.99 (0.28) ^a
60/40	49.03 (0.69) ^d	64.00 (0.57) ^a	55.43 (0.61) ^c	59.94 (2.32) ^b
70/30	49.01 (0.95) ^d	64.02 (1.78) ^a	52.94 (0.96) ^c	57.80 (1.91) ^b
80/20	42.55 (1.63) ^c	55.35 (1.23) ^a	48.63 (1.06) ^b	48.03 (0.97) ^b
90/10	49.82 (3.36) ^b	60.48 (2.31) ^a	55.07 (3.24) ^{ab}	60.13 (2.16) ^a
100/0	32.75 (1.58) ^b	40.02 (2.32) ^a	33.99 (3.26) ^{ab}	38.14 (3.49) ^{ab}

*DC could not be measured by the specific internal standard. Means followed by distinct letters in the same line are significantly different ($p < 0.05$).

Figure 2 - Linear regression analysis to obtain the relationship between DC and proportions of BisGMA/BisEMA blends.



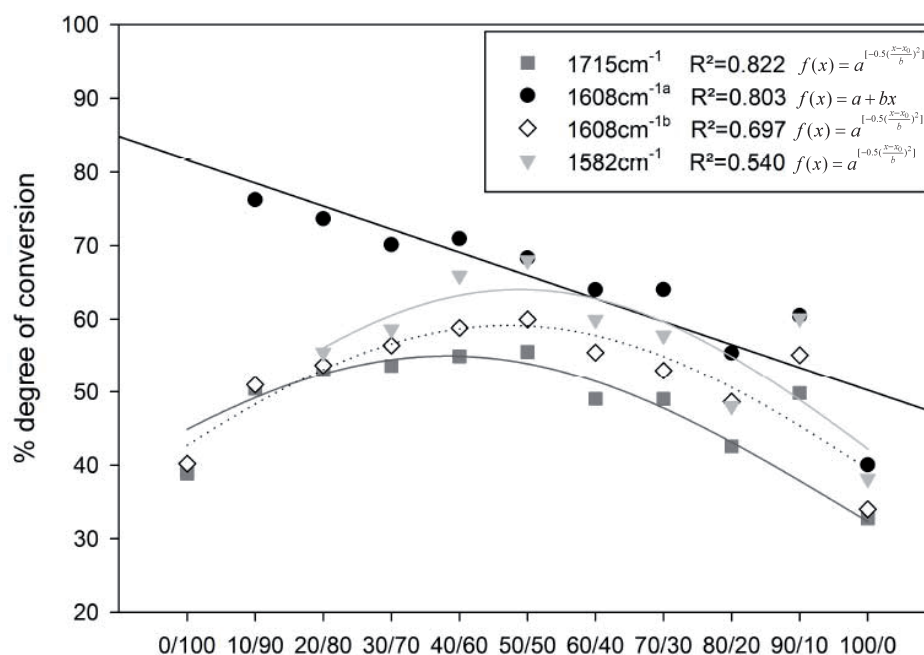
adequately fitted by linear regression ($R^2 > 0.9$; $p < 0.001$). Increasing the BisGMA/BisEMA ratio decreased the DC (Figure 2). Regardless of the internal standard peak or measurement baseline, the DC showed a strong association with the composition of the comonomer blend.

BisGMA/TEGDMA blends

BisGMA/TEGDMA blends could not be char-

acterized by linear regression, with the exception of the experiment using the 1608 cm^{-1a} standard peak and baseline method ($R^2 = 0.803$; $p < 0.001$). This set of experiments was better fit by Gaussian 3-parameter regression ($p_{1715 \text{ cm}^{-1}} < 0.001$; $p_{1608 \text{ cm}^{-1b}} = 0.004$; $p_{1582 \text{ cm}^{-1}} = 0.041$). Increasing the ratio of BisGMA/TEGDMA to 50/50 promoted an increase in DC. At BisGMA/TEGDMA ratios greater than 50/50, a decrease in DC was observed (Figure 3).

Figure 3 - Regression analysis to obtain the relationship between DC and composition of BisGMA/TEGDMA blends. The fitting equations for each plot are presented in the legend.



Discussion

This study aimed to evaluate how the measurement of DC via FTIR is influenced by the internal standard peak and baseline method. Comonomer blends with or without aromatic rings were tested. The DC of the comonomer blends varied from 32.75% to 78.50% as function of monomer composition and ratio. These results indicate that, contrary to our two null hypotheses, the internal standard and the baseline do, in some cases, affect measurements of DC.

The DC of BisGMA/BisEMA blends varied from 32.75% to 78.50%, presenting an indirect linear relationship to BisGMA concentration for all internal standards. The decrease in DC at larger BisGMA/BisEMA ratios can be attributed to differences in viscosity. Increasing the content of BisGMA can decrease the mobility of monomers into the polymerizing bulk.¹⁶ The results for these samples indicate that the blends composed of monomers with aromatic rings used in this study were not influenced by differences in the internal standard peak or baseline method.

The DC of BisGMA/TEGDMA blends ranged from 32.75% to 76.22%, presenting an indirect linear relationship to BisGMA concentration only for

the 1608 cm^{-1a} internal standard. Trends in DC for BisGMA/TEGDMA blends differed when the internal standard peak was varied from 1715 cm⁻¹ to 1608 cm^{-1b} and 1582 cm⁻¹. In general, the DC exhibited an initial increase as the BisGMA content was increased to 50 wt%, followed by a decrease as the BisGMA content was increased further. The results for BisGMA/TEGDMA show that the internal standards and baseline do influence the measured DC of comonomer blends containing monomers without aromatic rings (i.e., TEGDMA).

Our results are in accordance with those of a previous study that showed an increase in DC upon decreasing the BisGMA content in a BisGMA/TEGDMA blend.¹⁷ Thus, despite the large number of studies that determine DC via FTIR with the aromatic carbon-carbon peak (1608 cm⁻¹) as the internal standard, caution must be taken when using this method to find the DC of blends that contain monomers without aromatic rings. In the FTIR spectra of resins comprising a high content of monomers without aromatic carbon-carbon double bonds, the peaks at 1608 and 1582 cm⁻¹ have low or non-existent intensity, decreasing the reliability and reproducibility of DC measurements on these samples. However, most commercial methacrylate-based

dental materials do comprise monomers with aromatic rings; such monomers produce a stiff central core in the final polymer, increasing its mechanical strength.

Ideally, the DC of TEGDMA-rich blends (containing > 80% TEGDMA by weight) should be determined by other internal standard peaks besides 1608 cm⁻¹ due to the low intensity of this peak in the FTIR spectrum of such blends. For these blends, the 1715 cm⁻¹ peak, corresponding to the carbonyl C=O bond, showed reliable results. The lower DC values measured using the 1715 cm⁻¹ internal standard in comparison to the 1608 cm^{-1a} standard can be explained by the cyclization that occurs during TEGDMA polymerization. The TEGDMA molecule has a short and flexible chain that permits a methacrylate radical from one extremity to react with the methacrylate of another extremity, reducing the chain mobility and hindering the copolymerization of TEGDMA with BisGMA. This reaction forms an inhomogeneous polymer that presents a low DC.¹⁸

Unexpectedly, the 1608 cm^{-1b} internal standard yielded reasonable results for the DC of pure TEGDMA. This result should be viewed with caution, because this peak, theoretically, should not be present on the TEGDMA IR spectrum.

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In general, for both blend compositions, the measured DC values followed the following order: 1608 cm^{-1a} > 1582 cm⁻¹ > 1608 cm^{-1b} > 1715 cm⁻¹. Using the 1608 cm⁻¹ peak as internal standard, and determining its height by baseline method “a”, appears to be the best way to evaluate DC, yielding results that are comparable to those of other studies.^{19,20} Previous studies showed a direct linear proportional relationship between TEGDMA concentration and DC in dimethacrylate blends.²¹

Conclusion

The internal standard peak and baseline measurement affect the measured DC of methacrylate-based resins and its relationship to the comonomer blend composition, as determined by FTIR spectroscopy. The best internal standard for DC measurement is the 1608 cm⁻¹ peak, whose height is measured by baseline method “a”, for the comonomer blends that were used in this study.

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