

# Degree of Conversion Versus the Depth of Polymerization of an Organically Modified Ceramic Dental Restoration Composite by Fourier Transform Infrared Spectroscopy

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**ABSTRACT:** The evaluation of the degree of conversion (DC) as a function of the depth (1–4 mm) of an organically modified ceramic (ormocer) dental restoration composite activated by a conventional light-curing unit (450 nm, 21.2 J/cm<sup>2</sup>) was carried out. Fourier transform infrared spectroscopy was employed to measure DC at each depth with the ratio of the maximum height absorbance peaks at 1638 (variable band) and 1609 cm<sup>-1</sup> (reference band) before and after the polymerization reaction. The formulation was reconstituted to understand better the composite behavior. The organic and inorganic fractions were characterized by thermogravimetric analysis, X-ray fluorescence, proton nuclear magnetic resonance, and scanning electron microscopy. The DC values lay between 48 and 54%, seemed to be not sensitive to the depth of polymerization, and indicated a large amount of residual monomer. On the other hand, a continuous decrease in the Vickers microhardness (from 61 to 52)

was observed with an increasing depth of polymerization. This behavior could be attributed to differences in the crosslinking degree on the top and bottom surfaces of the polymerized samples. The material was a conventional dental restoration composite containing 26% monomer mixture (bisphenol A/dimethacrylate and triethylene glycol dimethacrylate), a small amount (2%) of an ormocer as a compatibilizing agent, and 72% inorganic filler (barium sulfate and aluminum silicate). The low DC values could be ascribed to several factors, such as the monomer viscosities, amounts, and types, the average sizes and distributions of the fillers, and the large difference between the refractive indices of the organic and inorganic constituents. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 325–330, 2007

**Key words:** composites; FTIR; hardness; NMR; thermogravimetric analysis (TGA)

## INTRODUCTION

Dental composite restorative materials have the capability of effectively reproducing the form, texture, and color of dental elements. They are frequently employed as replacements for traditional metallic restoration, which, though mechanically and chemically resistant and possessing an estimated lifetime of approximately 20 years, does not offer the same aesthetic appearance. Polymer-based dental composites present additional advantages such as easy handling and a prompt photopolymerization reaction.<sup>1</sup>

Nevertheless, several problems concerning the lack of mechanical resistance mainly associated with restoration in posterior teeth and heterogeneity in the depth of polymerization frequently are mentioned as drawbacks for the use of polymer restoration dental composites as repairing materials.<sup>2</sup> Both problems are related to the polymerization process responsible for the formation of the crosslinking network that provides mechanical resistance and hardness to the final composite.<sup>3</sup> The degree of conversion (DC) of conventional dental composites lies in the range of 50–60% and depends on several factors, such as the organic and inorganic components, specimen geometry, amount and type of the photoinitiator, and light intensity.<sup>4–6</sup> DC can be significantly affected by the distance from the light source, and through the depth, light can be scattered between resin and particle interfaces and be absorbed by both; this results in a continuous decrease in the light intensity during the cure reaction. Therefore, a lower DC value is expected to cause a premature failure of the restoration because of increasing wear, precocious staining, and marginal microleakage.<sup>7,8</sup>

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Numerous attempts have been carried out to minimize such problems, most of them relying on changes in the type (crystalline quartz, colloidal or pyrolytic silica, and barium glass), size, size distribution, and amount of the inorganic particles employed as reinforcements for the composites.<sup>9</sup> Since Bowen<sup>10</sup> introduced in the 1960s bisphenol A/dimethacrylate (BisGMA), few structural variations in the organic matrix of dental composites have been proposed until recently with the advent of organically modified ceramics (ormocers).<sup>11</sup> An ormocer is a hybrid ceramic composite in which the main chain is formed by polysiloxane linkages containing pendant unsaturated carbon chain molecules.<sup>12</sup> Such structures can be considered prepolymers and are therefore less susceptible to polymerization contraction because of a lower number of polymerization sites. Additionally, an ormocer is expected to present higher biocompatibility than standard BisGMA-based composites as well as lower sensitivity to the polymerization depth.<sup>13–15</sup> Although ormocers are very promising, few investigations have confirmed the potential of ormocers as biomaterials or low-contraction materials applied to teeth restoration. Kim and coworkers<sup>16,17</sup> studied the degree of conversion of an ormocer by Fourier transform infrared (FTIR) for optical applications as a photonic material and therefore in the absence of inorganic fillers. Additionally, the material was employed as a thin film, and this suggested no dependence on the film thickness or depth of polymerization.

In this study, FTIR was employed to evaluate DC as function of the depth of polymerization of a commercial ormocer dental restoration composite. The experimental procedure (light wavelength, depth, exposure time, etc.) was similar to that performed for the DC determination of conventional dental fillings based on BisGMA. To understand better the results, the formulation was reconstituted with techniques such as thermogravimetric analysis (TGA), X-ray fluorescence (XRF), proton nuclear magnetic resonance (<sup>1</sup>H-NMR), and scanning electron microscopy (SEM). The Vickers microhardness (VMH) was measured and did not show any relationship with DC.

## EXPERIMENTAL

### Materials

A commercial ormocer dental restoration composite named Admira (shade A1, batch number 00201), manufactured by Voco (Cuxhaven, Germany), was evaluated. According to the supplier, the composite was 78% inorganic particles (barium and aluminum silicate) with an average size of 0.7  $\mu\text{m}$ , and the organic fraction was composed of BisGMA, triethylene glycol dimethacrylate (TEGDMA), and urethane dimethacrylate (UDMA).

**TABLE I**  
Selected <sup>1</sup>H-NMR Chemical Displacements of Commercial Monomers<sup>18</sup>

Monomer	<sup>1</sup> H-NMR
BISGMA	6.96 and 7.2 (8H, aromatic ring)
TEGDMA	3.72 (4H, CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> )
UDMA	4.7–5.2 (2H, NH urethane)

### Specimen preparation

Specimens were prepared by the insertion of the composite into a stainless steel, two-part mold with a 10-mm diameter and a depth varying from 1 to 4 mm; there were five specimens in each. The bottom of each mold was put on a black-painted glass slide to prevent light scattering. Then, the composite was inserted into the mold by one increment, the top surface being covered with a glass plate to avoid contact with oxygen. After that, the cure unit (400 Demetron, Optilux; 450 nm, 0.53  $\pm$  10 W/cm<sup>2</sup>, and 40 s) was placed perpendicularly on the assembly, and polymerization was carried out. Finally, the sample was kept in an oven, without light, at 37°C for 24 h.

### TGA

The quantitative determination of the organic and inorganic portions of the composite was performed in a PerkinElmer TGA-7 (Norwalk, CT) with 6 mg of each sample, and the analysis was conducted at 30–700°C at 10°C/min under a nitrogen atmosphere.

### XRF analysis

The qualitative and quantitative determination of the inorganic portion of the composite was carried out by XRF with a Rigaku model RIX 3100 instrument (Osaka, Japan). Two grams of ash from the burnt composite was pressed to form a disk and was used to scan light and heavy elements.

### <sup>1</sup>H-NMR analysis

<sup>1</sup>H-NMR was performed in a Varian Mercury 300. The sample was dissolved in deuterated chloroform at 2% (w/v) and analyzed at 25°C and 300 MHz. Commercial monomer samples of BisGMA, TEGDMA, and UDMA were analyzed under the same conditions, and the pertinent chemical displacement (Table I) was selected.<sup>18</sup> The quantitative calculations of the organic portion of the composite were performed, and the peak integration, the number of hydrogen atoms representative for each chemical displacement, and the molecular mass of the monomers were taken into account. For each monomer, the peak area of the selected chemical displacement was multiplied by its molecu-

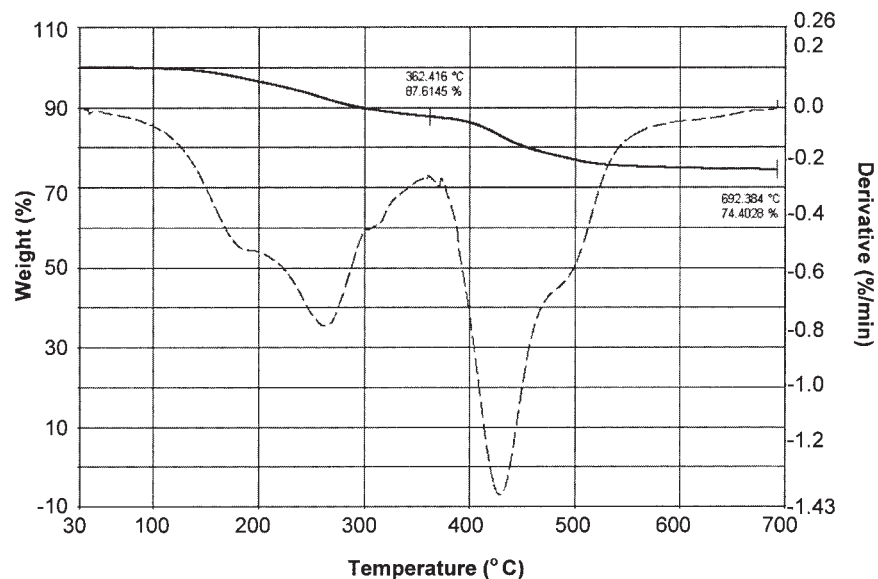


Figure 1 (—) TGA curve and (- - -) derivative curve ( $dm/dT$ ) of the composite.

lar mass. These products were named  $x$  and  $y$  for BisGMA and TEGDMA, respectively. The proportion of each monomer was obtained by the division of  $x$  or  $y$  by the sum of  $x$  and  $y$ .

#### FTIR analysis

The FTIR analysis was conducted in a PerkinElmer 1720 X spectrometer. The nonpolymerized sample was dissolved in chloroform. The solution was poured onto a KBr cell and evaporated, and the assembly was put in the support. The spectrum was obtained from 40 scans at a  $2\text{-cm}^{-1}$  resolution. For the polymerized samples, about 2.0 mg of the material was mixed with KBr powder, and five transparent disks were obtained for each depth. The FTIR spectra were obtained as mentioned previously. The height of the selected peak absorptions at  $1638\text{ cm}^{-1}$  (C=C of the methacrylate group) and  $1609\text{ cm}^{-1}$  (C=C of the aromatic ring), with the region of  $1800\text{--}1500\text{ cm}^{-1}$  as the baseline, was measured. After that, their ratio was calculated, and DC was determined with the following equation:<sup>19</sup>

DC (%) =

$$100 - \frac{[\text{abs}(\text{C}=\text{C})_{1638} / \text{abs}(\text{C}=\text{C})_{1609}]_{\text{polymerized}}}{[\text{abs}(\text{C}=\text{C})_{1638} / \text{abs}(\text{C}=\text{C})_{1609}]_{\text{monomer}}} \times 100$$

where  $[\text{abs}(\text{C}=\text{C})_{1638} / \text{abs}(\text{C}=\text{C})_{1609}]_{\text{polymerized}}$  is the ratio of the C=C absorptions of the methacrylate group and the C=C absorption of the aromatic ring after polymerization and  $[\text{abs}(\text{C}=\text{C})_{1638} / \text{abs}(\text{C}=\text{C})_{1609}]_{\text{monomer}}$  is the ratio of the C=C absorptions of the methacrylate group and the C=C absorption of the aromatic ring before polymerization.

#### SEM

The morphology of the polymerized composite was determined with a Zeiss DSM 940A scanning electron microscope. A small specimen of the sample was inserted into an epoxy mold, polished, and sputtered with a thin layer of gold. The voltage was 15 kV, and the flat and transversal surfaces of the sample were observed.

#### VMH

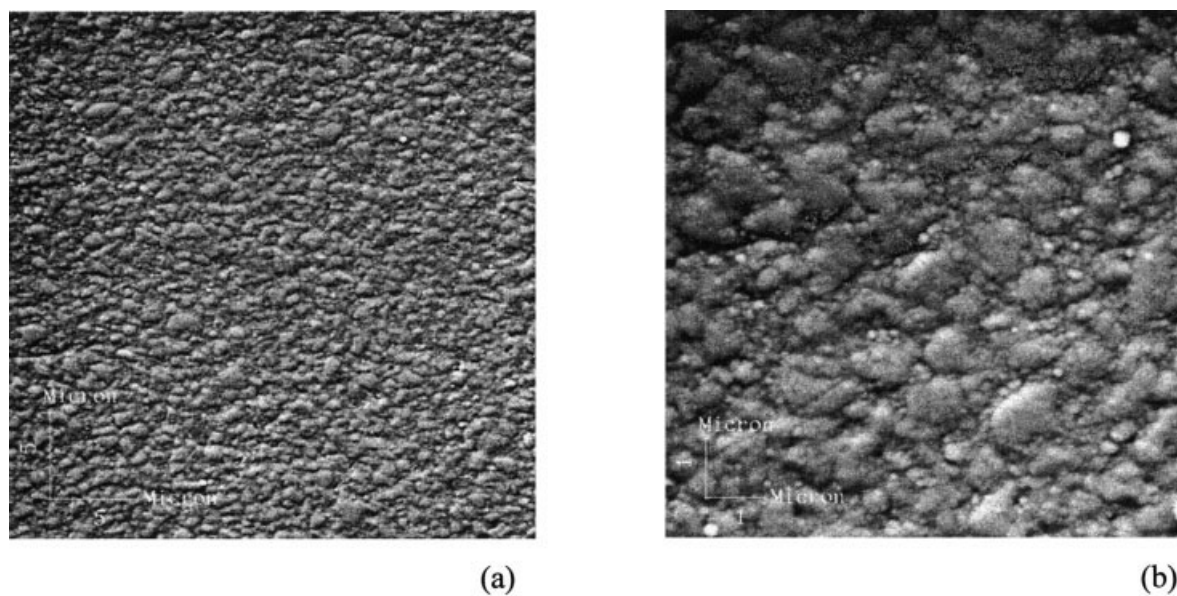
The determination of VMH was performed in a Leitz Duomet 2 (Wetvlar, Germany) on the surface at a depth of 0–4 mm. In all cases, a load of 50 g was applied for 30 s. At least 16 indentations were performed in each specimen, with the distance kept at 2.5 times the diagonal length between two impressions. After that, the indenter was removed, and the diagonal was measured as VMH.

## RESULTS

The TGA and derivative thermogravimetric curves are shown in Figure 1. Two regions can be clearly distinguished, from 150 to 360°C and from 360 to 500°C, indicating a two-step degradation process. The weight loss after each step was 12.4 and 13.2%, respectively, and represents the organic portion, whereas the inert residue (74.4%) corresponds to the inorganic portion.

The XRF analysis showed silicon dioxide ( $\text{SiO}_2$ ; 56.2%), barium oxide ( $\text{BaO}$ ; 33.8%), and aluminum trioxide ( $\text{Al}_2\text{O}_3$ ; 10.0%) in the ash of the burnt composite.





**Figure 2** SEM photomicrograph of the polymerized composite a) 1 K and b) 10 K magnification.

Figure 2(a,b) shows SEM photomicrographs of the polymerized samples at different magnifications. The predominant size particle is around  $1\ \mu\text{m}$ , but there is also a broad distribution revealed by a notable number of submicrometer particles.

The  $^1\text{H-NMR}$  spectrum of the organic fraction of the composite showed chemical displacements at 0–3.5, 3.5–5.5, 5.5–6.5, and 6.5–7.5 ppm ascribed to hydrogen linked to aliphatic carbon, hydrogen linked to carbon–oxygen linkage, hydrogen of unsaturated carbon, and hydrogen linked to the aromatic ring, respectively. When the sample spectrum was compared with ones of known samples of commercial monomers, we detected chemical displacements ascribable to BisGMA and TEGDMA but not to UDMA, as reported by the supplier. The composition of the organic portion was 65.5% BisGMA and 34.5% TEGDMA. The percentages were normalized with respect to the weight of the organic portion in the composite, and this gave values of 16.8% BisGMA and 8.8% TEGDMA.

The FTIR maximum peak heights at 1638 and 1609  $\text{cm}^{-1}$ , their ratio, and the average ratio and standard deviation of the composite before and after polymerization are listed in Table II. The average DC calculated according to the equation and standard deviation for each depth is shown Table III. The DC values were between 48 and 54%.

The VMH values as function of the depth of polymerization are listed in Table IV, which shows values between 61 and 52.

## DISCUSSION

The two decays in the TGA curves represented not only a single weight loss but also a complex burning

process evidenced by a large temperature windows and the presence of small shoulders. From the curves, it is not possible to state if each step is related to the burning of each monomer alone or if both components lose their methacrylate portion during the first decay and the remaining portion degrades during the subsequent step. A more accurate study must be carried out. According to TGA, the composite is 26% organic and 74% inorganic; this confirms that it is a high-density composite.

According to NMR, the chemical displacement characteristic of UDMA was not observed because its concentration was below 0.5% and was not detectable. BisGMA (16.8%) was the main component, whereas TEGDMA (8.8%) was the comonomer. The aliphatic monomer (TEGDMA) acted as a diluent for the aromatic one (BisGMA), increasing its handling. Their ratio was around 2. The concentration of the organic portion (25.6%) found by NMR corroborated the TGA one.

With respect to the inorganic portion, the ash content from the burnt composite with an oxidizing atmosphere was 72%. The difference from the TGA residue (74% in a nitrogen atmosphere) suggested that the composite contained about 2% ormocer, which was more thermally stable, acting as a compatibilizing agent. On the basis of the XRF analysis, it was possible to infer that the filler contained 51.4% barium sulfate and 48.6% aluminum silicate (normalized to 37 and 35%, respectively) in the inorganic portion. These two fillers are commonly used in conventional dental restoration composites.<sup>20,21</sup>

With respect to FTIR, the DC values showed a slight variation with the depth (48–54%), and this indicated that DC was not sensitive to the depth. On the other

**TABLE II**  
**FTIR Maximum Peak Heights, Ratios, and Average Ratios of the Composites Before and After Polymerization at Different Depths**

Depth (mm)	Specimen	Maximum peak height		Ratio (1638/1609)	Average ratio
		At 1638 cm <sup>-1</sup>	At 1609 cm <sup>-1</sup>		
NP	1	0.1881	0.0593	3.1720	3.0667 ± 0.0084
	2	0.0739	0.0248	2.9798	
	3	0.1454	0.0477	3.0482	
0	1	0.0388	0.0261	1.4865	1.3970 ± 0.0720
	2	0.1184	0.0917	1.2911	
	3	0.0951	0.0703	1.3527	
	4	0.1149	0.0827	1.3893	
	5	0.1310	0.0894	1.4653	
1	1	0.0548	0.0548	1.000	1.4498 ± 0.2298
	2	0.0732	0.0466	1.5708	
	3	0.0617	0.0405	1.5234	
	4	0.0620	0.0377	1.6445	
	5	0.0580	0.0384	1.5104	
2	1	0.0677	0.0429	1.5780	1.5928 ± 0.0344
	2	0.1117	0.0704	1.5877	
	3	0.1240	0.0767	1.6166	
	4	0.0970	0.0591	1.6412	
	5	0.1374	0.0892	1.5403	
3	1	0.0866	0.0526	1.6463	1.5494 ± 0.2281
	2	0.0647	0.0362	1.7872	
	3	0.0732	0.0419	1.7470	
	4	0.0627	0.0522	1.2011	
	5	0.0788	0.1317	1.3656	
4	1	0.0635	0.0430	1.4767	1.4883 ± 0.0186
	2	0.0862	0.0584	1.4760	
	3	0.1055	0.0708	1.4901	
	4	0.1085	0.0712	1.5238	
	5	0.0963	0.0653	1.4747	

NP = composite that was not polymerized.

hand, the DC values of conventional dental restoration composites frequently decrease with increasing depth.<sup>20,21</sup> The behavior of DC could be ascribed to a compatibilizing effect provided by ormocer molecules in the composite. Furthermore, the SEM photographs showed that the filler particles were well dispersed in the matrix and joined among them. The lower size particles seemed to agglomerate. Voids or microcracks were not detected, and this indicated good compatibility between the organic and inorganic portions.

With respect to the hardness, the VMH values decreased continuously with increasing depth. There was not a direct relationship between the DC and

hardness. A possible reason for this behavior could be that DC depends intrinsically on the extent of the polymerization reaction, whereas the hardness depends on the extent of the reaction and the degree of crosslinking produced during the monomer curing process.

Among other factors, the type, amount, particle size and distribution, and monomer viscosities could contribute to low values of DC. If one considers that the particle size is around 1 μm, particles with lower dimensions agglomerate, and the wavelength of the incident light is 0.45 μm, large light scattering, leading to decreasing DC values, is ex-

**TABLE III**  
**Average DC Values of the Composites After Polymerization at Different Depths**

Depth (mm)	Specimen					Average DC	
	1	2	3	4	5		
DC (%)	0	51.52	57.90	55.89	54.70	52.22	54.45 ± 2.63
	1	67.39	48.78	50.32	46.37	50.75	52.70 ± 8.38
	2	48.54	48.26	47.28	46.48	49.77	48.07 ± 1.25
	3	46.31	41.72	43.03	60.83	55.47	49.47 ± 8.32
	4	51.85	51.87	51.41	50.31	51.91	51.47 ± 0.68

**TABLE IV**  
**VMH Values of the Composites After Polymerization**  
**at Different Depths**

Polymerization depth (mm)	VMH
0.0	61.0 ± 4.5
1.0	59.9 ± 3.9
2.0	56.7 ± 5.4
3.0	53.8 ± 5.4
4.0	52.1 ± 3.4

pected. A similar effect is caused by the refractive index (RI) of the components. The RI values of barium sulfate, aluminum silicate, TEGDMA, and BISGMA are 1.637, 1.660, 1.460, and 1.549, respectively.<sup>22</sup> The significant differences among them influence the light transmission, resulting in a great scattering of light and low DC values even on the top surface. With respect to the organic portion, the high viscosity (500,000–800,000 mPa s) of the main monomer (BisGMA), even diluted with TEGDMA (10,000 mPa s), renders difficult the diffusion of the monomer to the centers of chain growth and then contributes to the depression of DC.<sup>23</sup> The subject needs a systematic study to investigate the actual effect of each component individually on DC. Then, considering the contents of the organic and inorganic portions of the dental restoration composite, we can state that the material is a conventional dental filling containing a small amount of an ormocer as a compatibilizing agent.

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